PHYSICO-CHEMICAL STUDIES ON SOME METALLIC CORROSION INHIBITORS

SUMMARY

THESIS

SUBMITTED FOR THE AWARD OF THE DEGREE OF

Doctor of Philosophy

IN

APPLIED CHEMISTRY

BY

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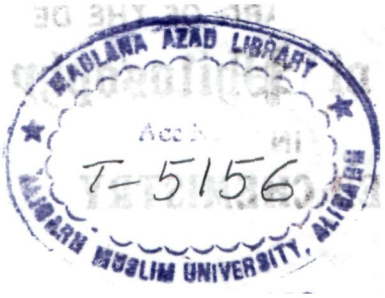
1998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SUMMARY

Corrosion is a major problem in several industries. It causes enormous economic wastage of metallic materials, which leads to heavy economic losses all over the world. In India the monetary losses due to corrosion have been estimated as high as Rs. 25,000 crores per year.

Among the available methods of preventing corrosion the use of inhibitors is one of the most promising methods, particularly for closed systems. Due to ease of application and cost effectiveness it has attracted a great deal of attention of corrosion scientists and engineers all over the world.

Mild steel is one of the most important engineering metal, which due to its low cost and excellent mechanical properties is widely used as a construction material. The mild steel is severely attacked in acid solutions, as it usually comes in contact with HCl and H_2SO_4 in various industries during pickling cleaning of industrial equipments and acidization of oil wells etc. Inhibited acid solutions are commonly used to reduce the corrosive attack of acid on metals. The use of inhibitors is specific for different systems and thus it needs to be studied thoroughly.

The research work described in the thesis deals with the study of nitrogen and sulphur containing organic compounds as corrosion inhibitors for mild steel in 1N, 3N and 5N HCl at 40°C. Some organic compounds have been evaluated in 1N HCl and 1N H_2SO_4 at room temperature. The molecular structures and names of these compounds are given in Table 1.0. The techniques such as weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy, hydrogen permeation, auger electron spectroscopy and scanning electron microscopy have been used in these studies on corrosion inhibition.

The thesis comprises of three chapters. The first chapter presents a general introduction which highlights the economic and technological importance of corrosion. Theories of corrosion have also been described, which help in understanding the mechanism of corrosion. Special attention has been given to explain the mode of action of inhibitors towards corrosion control. The account of various techniques used for investigating corrosion inhibitors have been discussed briefly. A survey of the literature on corrosion inhibitors for mild steel in acid solution has also been given.

The aims and objectives have also been mentioned.

The description of inhibitor synthesis and the details of experimental techniques such as weight loss, potentiodynamic polarization, AC impedance, hydrogen permeation, auger electron spectroscopy and scanning electron microscopy used in these studies are given in second chapter.

The third chapter describes the discussion of results obtained during these studies. The compounds of which inhibitive action has been studied are tabulated. Their inhibiting action have been discussed separately in following sections :-

(i) Macrocyclic compounds (ii) Substituted Thiobisformamidines

(iii) Substituted Dithiobiurets (iv) Substituted Thiocarbohydrazides

The results of these investigations revealed the fact that all of the macrocyclic compounds inhibit the mild steel corrosion effectively in acid solutions. The maximum value of inhibition efficiency is achieved at 500, 700 and 2000 ppm in 1N, 3N and 5N HCl at 40°C in the following order:-

PTAT > PTAB > POAB

The difference in inhibitive action of macrocyclic compounds has been explained in terms of the number and nature of heteroatoms, present in them. The effect of macrocyclic compounds studied in 1N HCl and H_2SO_4 at room temperature (35± 2°C) exhibited inhibition efficiency in the following order:-

TBOAD > DBOAD > BMOAT > BOAH > MOAT >OAH

The difference in inhibition efficiency of these compounds can be explained on the basis of the number of aromatic rings present in them. TBOAD contains four aromatic rings and so it has exhibited highest inhibition efficiency, whereas OAH showed lowest inhibition efficiency due to the absence of aromatic ring in it.

The inhibition efficiencies of substituted thiobisformamidines in 1N, 3N and 5N HCl follow the order:-

CPTBF > ATBF > TTBF > PTBF

Among these four compounds chloro derivative showed highest inhibition efficiency due to its high dipole moment than other compounds. The better performance of ATBF than TTBF has been explained on the basis of Pearson's hard and soft acid

base principle (HSAB). The order of inhibition efficiency of different dithiobiurets has been found to be as follows:-

APDTB > TPDTB > DPDTB >CPDTB

The better performance of APDTB may be attributed to the presence of electron releasing $-OCH_3$ group. The lowest value of inhibition efficiency for CPDTB among the studied compounds can be explained on the basis of – I effect (electron withdrawing inductive effect) of chloro group on the reaction site thus showing less adsorption and less inhibition of corrosion. The inhibition efficiency values of substituted thiocarbohydrazides in 1N, 3N and 5N HCl solutions follow the order:-

CTCH > VTCH > STCH > FTCH > BTCH

CTCH exhibited highest inhibition efficiency among the studied thiocarbohydrazides which can be explained due to the presence of an additional π bond between carbon atoms –C = C conjugated to azomethine group (–C = N) . VTCH shows better inhibition efficiency than STCH due to the presence of an additional electron releasing methoxy group (– OCH_3). STCH is found to exhibit superior inhibition efficiency than FTCH due to presence of –OH group. The better performance of FTCH than BTCH may be attributed to the presence of lone pairs of electrons on oxygen atom through which it can adsorb more strongly than BTCH leading to high inhibition efficiency.

The effect of temperature, immersion period and inhibitor concentration has also been studied on inhibition efficiency of all the investigated compounds. The following conclusions have been drawn:-

1. Inhibition efficiency of Thiocarbohydrazides, Thiobisformamidines and Dithiobiurets increases on increasing the temperature from 40-70°C, whereas the inhibition efficiency of macrocyclic compounds decreases on rise in temperature.
2. The inhibition efficiency of all the compounds increases on increasing the immersion period (24 - 96 hours) as well as inhibitor concentration.
3. The inhibition efficiency of these compounds decreases on increasing the acid concentration from 1N - 5N.

An interesting feature of these investigations is that inhibition efficiency of all the tested compounds increased on the addition of small amount of KI to acid solutions due to synergism. The synergistic effect has also been found to be more pronounced in case of substituted dithiobiurets.

Sixteen compounds out of twenty two were evaluated as corrosion inhibitors in 5N HCl in 70°C. The compound CTCH has given highest inhibition efficiency of 99% among the tested compound at a concentration of 500 ppm in 5N HCl at 70°C.

Potentiodynamic polarization studies reveal that all the tested inhibitors are mixed inhibitors except CTCH, FTCH, TPDTB and CPDTB, which showed predominantly cathodic behavior in 1- 5N HCl. The compounds BMOAT, MOAT, BOAH and OAH exhibited mixed nature in 1N HCl and predominantly cathodic behavior in 1N H_2SO_4.

Selected compounds were evaluated through electrochemical impedance spectroscopic technique in 1N HCl solution. CTCH has been found to be more effective inhibitor as it increased the R_t value more than other compounds.

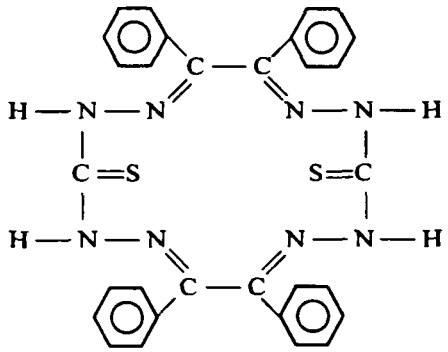
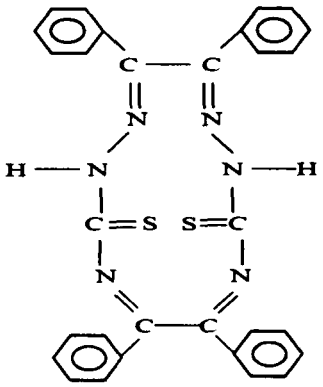
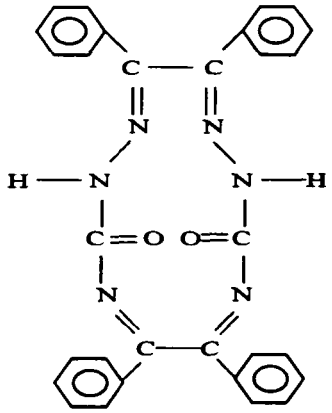
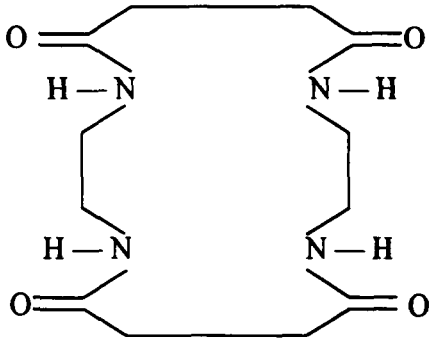
The compounds selected for hydrogen permeation tests were found to reduce the hydrogen permeation current in 1N HCl. Maximum reduction in hydrogen permeation current was observed in case of CTCH and minimum in case of PTAB.

The order of inhibitive performance of various classes of organic compounds examined in the present investigations is :-

Dithiobiurets > Thiocarbohydrazides > Thiobisformamidines > Macrocyclic compounds

The results of auger electron spectroscopy (AES) studies show that the adsorption of inhibitor molecules on the metal surface occurs through heteroatoms such as N, S or O atoms. The better appearance of mild steel surface in inhibited acid solution than in plain acid solutions as evident from scanning electron microscopic (SEM) studies further supports the fact that inhibitor molecules are adsorbed over the steel surface and prevent the attack of corrosive acid solutions on the steel surface.

TABLE 1.0:- NAME AND STRUCTURAL FORMULAE OF THE INHIBITORS USED

S.No.	STRUCTURAL FORMULA	DESIGNATION AND ABBRIVIATION
1		Tetraphenyl-dithia-octaaza-cyclotetradecane hexaene (PTAT)
2		Tetraphenyl-dithia-hexaaza-cyclobidecane hexaene (PTAB)
3		Tetraphenyl-dioxo-hexaaza-cyclobidecane hexaene (POAB)
4		2,5,10,13-tetraoxo-1,6,9,14-tetraazacyclohexadecane (OAH)

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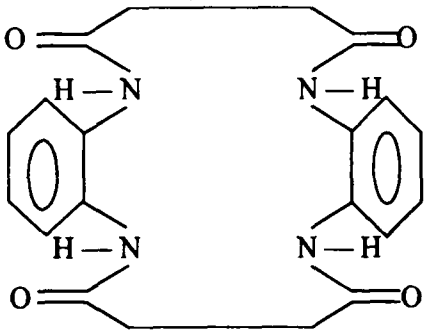
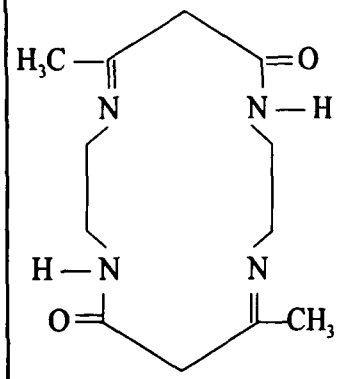
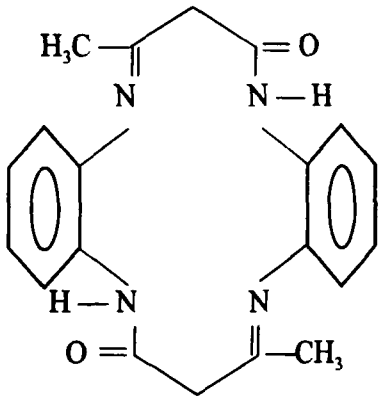
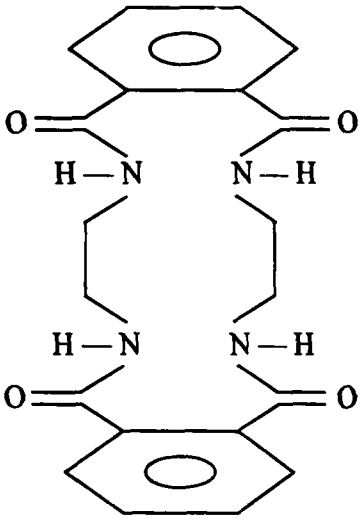
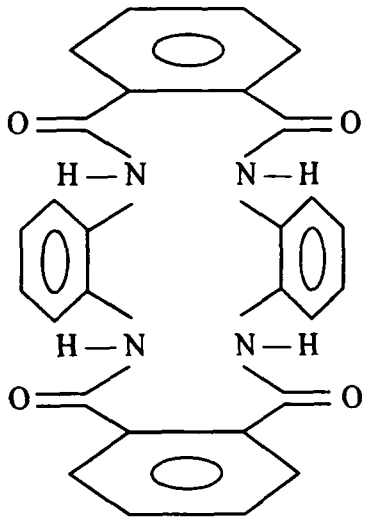
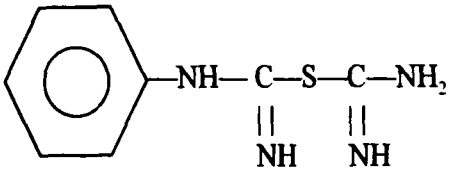
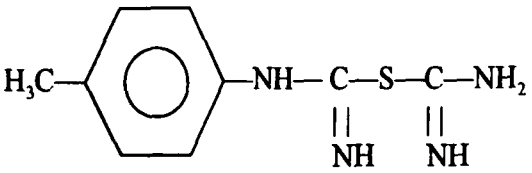
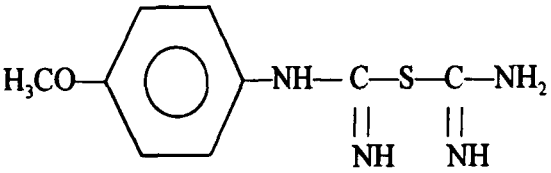
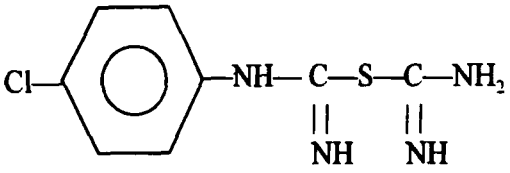
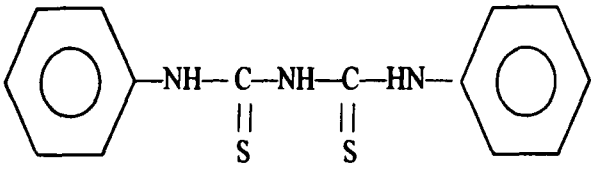
S.No.	STRUCTURAL FORMULA	D ESIGNATION AND ABBRIVIATION
5		7,8:15,16-dibenzo-2,5,10,13-tetraoxo-1,6,9,14 -tetraazacyclo-hexadecane (BOAH)
6		7,14-dimethyl-5,12-dioxo-1,4,8,11-tetaazacyclotetradeca-1,7-diene (MOAT)
7		2,3:9,10-dibenzo-7,14-dimethyl-5,12-dioxo-1,4,8,11-tetraaza-cyclotetradeca-1,7-diene (BMOAT)
8		3,4.11,12-dibenzo 2,5,10,13-tetraoxo-1,6,9,14-tetraazacy-clohexadecane (DBOAD)

Contd —

S.No.	STRUCTURAL FORMULA	DESIGNATION AND ABBRIVIATION
9		3,4:7,8:11,12:15,16-tetrabenzo-2,5,10,13-tetraoxo-1,6,9,14-tetraazacyclohexadecane (TBOAD)
10		Phenyl Thiobisformamidine (PTBF)
11		Tolyl Thiobisformamidine (TTBF)
12		Anisidyl Thiobisformamidine (ATBF)
13		4-cholrophenyl Thiobisformamidine (CPTBF)
14		1,5-diphenyl-2,4-dithiobiuret (DPDTB)

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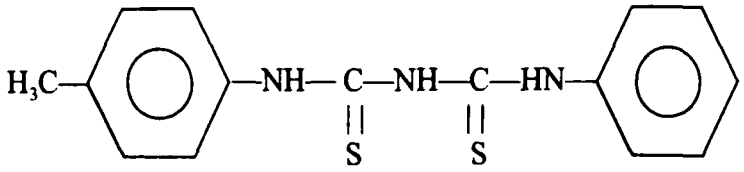
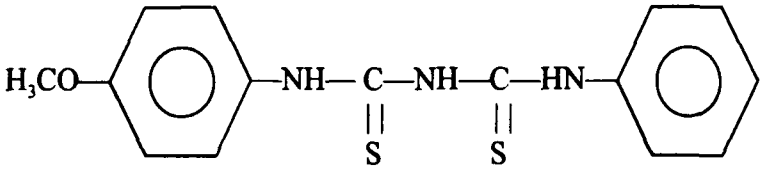
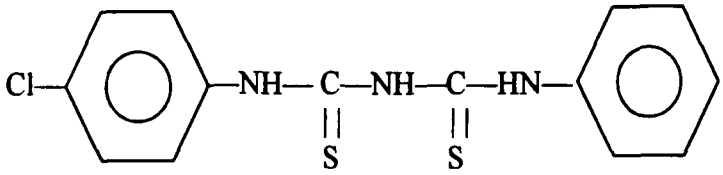
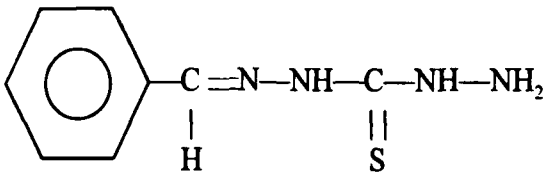
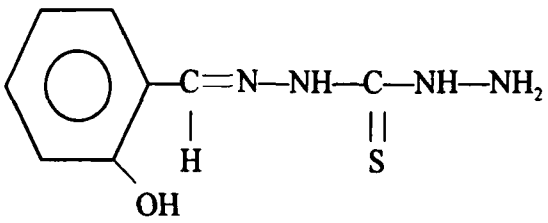
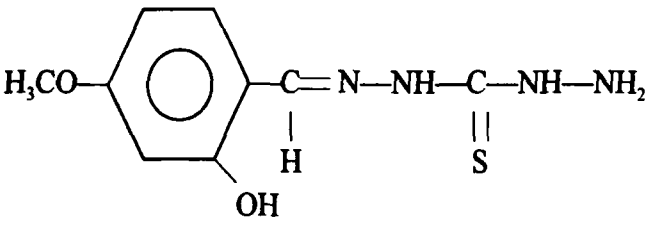
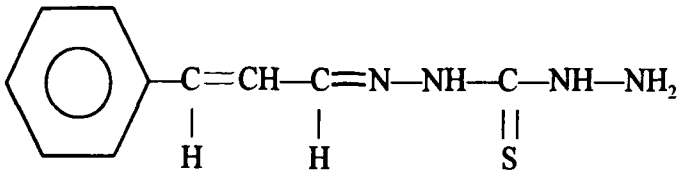
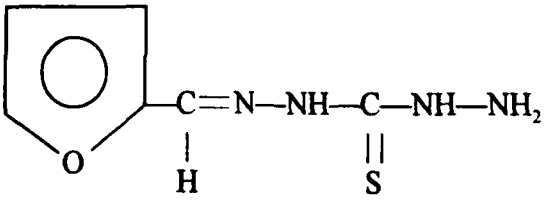
S.No.	STRUCTURAL FORMULA	DESIGNATION AND ABBRIVIATION
15		1-tolyl-5-phenyl- 2,4 -dithiobiuret (TPDTB)
16		1-anisidyl-5-phenyl-2,4-dithiobiuret (APDTB)
17		1-chlorophenyl-5-phenyl-2,4 dithiobiuret (CPDTB)
18		1-benzylidene-3-thiocarbohydrazide (BTCH)
19		1-salicylidene-3-thiocarbohydrazide (STCH)
20		1-vanillidene-3-thiocarbohydrazide (VTCH)
21		1-cinnamylidene-3-thiocarbohydrazide (CTCH)
22		1-furfurylidene-3-thiocarbohydrazide (FTCH)

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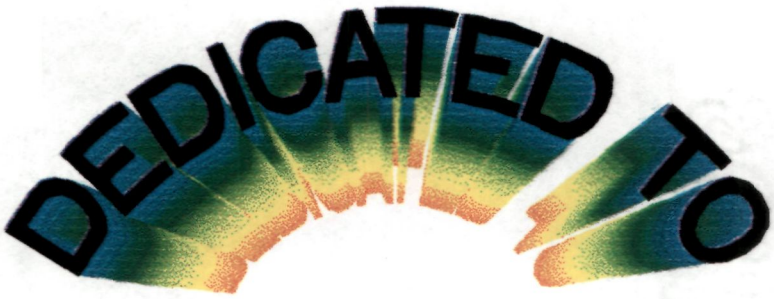

MY GRANDMOTHER

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Aligarh Muslim University, Aligarh - 202002 (India)

Date: 14.12.98

Certificate

This is to certify that, the work incorporated in this thesis entitled, "Physico-Chemical Studies on Some Metallic Corrosion Inhibitors" is the original contribution of Miss. Jaya Rawat, carried out under our supervision and guidance. The work submitted in this thesis has not been submitted elsewhere for any degree and is suitable for submission to the award of Ph.D. degree.

Dr. M.A. Quraishi
(SUPERVISOR)

Prof. Mohammad Ajmal
(CO-SUPERVISOR)

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God (success) & Teacher both are standing in front of me, to whom should I express my gratitude first. I am grateful to my supervisors Prof. Mohammad Ajmal & Dr. M.A. Quraishi because of their precious guidance and support I am able to meet God (success).

Research work is not an easy task. It needs a lot attention and cooperation from every corner. Prof. H.S. Rathore, Chairman of Department of Applied Chemistry is one from whom I got constant support throughout my work. Along with Prof. Rathore, I am also thankful to Dr. S.V.K, Iyer, Dr. S. Muralidharan & Dr. V. Chari, CECRI, Karaikudi.

I am profoundly grateful to my colleagues, friends & family members for their encouragement and day to day cooperation.

Thanking would be a negligible thing for my parents whose Love, Affection & Cooperation have been foundation of my success.

Jaya Rawat

Jaya Rawat

CONTENTS

The deterioration or destruction of materials (metals) under the chemical or electrochemical action of the surrounding environments is called Corrosion [1]. It is generally accepted now, that corrosion is a reversion or a partial reversion from the metastable condition of the metal to a stable condition of the mineral accompanied by the reduction in the free energy of the system. Metals such as gold and platinum remain unaffected for centuries while others like copper, iron, aluminium etc. are likely to change in to their compounds when kept exposed to aggressive environment. The later metals tend to revert back to the combined state forming oxides, sulphides, carbonates etc. The deterioration by physical causes is not corrosion but it is described as erosion, galling or wear.

1.1 ECONOMIC LOSSES DUE TO CORROSION

Corrosion is a big menace to the economy of the country. The loss due to corrosion has been estimated to be of the order of 2 - 5% of the GNP of any country. In India the losses have been estimated approximately of 25,000 crores rupees per year due to the impact of corrosion according to News letter NACE, India [2].

1.2 CLASSIFICATION OF CORROSION

Corrosion has been classified in many different ways as low and high temperature corrosion, direct oxidation and electrochemical corrosion etc. Generally corrosion is classified as : –

(1) Dry or Chemical Corrosion

(2) Wet or Electrochemical Corrosion

1.2.1 DRY OR CHEMICAL CORROSION

This occurs in the absence of a liquid phase or above the dew point of the environment by the metal / gas or metal / vapour reactions involving nonmetals such as oxygen, halogen, hydrogen sulphide, sulphur vapours etc. High temperature oxidation of metals and tarnishing of metals like Cu, Ag etc. fall into this category.The

initial oxidation of the metal, reduction of non metal and formation of compound must occur at one and the same place at the metal /nonmetal interface .

1.2.2 WET OR ELECTROCHEMICAL CORROSION

In wet corrosion the oxidation of the metal and reduction of a species in solution occurs at different areas on the metal surface (local cathodic and anodic sites) with consequent electron transfer through the metal from anode (metal oxidised) to the cathode (electron acceptor reduced). The thermodynamically stable phases formed at metal / solution interface in the form of solid compound or hydrated ions (Cations or anions) may be transported away from the interface by migration or diffusion or convection. The corrosion of steel in water is its example.

1.3 FACTORS INFLUENCING CORROSION

The major important factors which influence the corrosion process are :– nature of the metal and environment, electrode potential, temperature, aeration, corrosion products formed, agitation, concentration of various ions in the solution, pH of the solution, hydrogen overpotential and amount of dissolved oxygen etc.

Apart from these factors there are some other factors also such as presence of bacteria and depth of immersion and presence of dissolved salts in sea water electrical resistivity, porosity and moisture in underground corrosion of gas pipelines etc., which influence the process of corrosion.

1.4 VARIOUS FORMS OF CORROSION

Corrosion can manifest in different forms [3]. It is desirable to know the form of corrosion since it will help in identification of the cause of corrosion and thereby the effective method can be chosen to prevent it. Except the general or uniform corrosion all the other forms are insidious in nature, the main forms of corrosion are given as under : –

1.4.1 GENERAL CORROSION OR UNIFORM ATTACK

This is the most common type of corrosion in which the corrosion is uniform over the entire exposed surface e.g. Water tanks subjected to the atmospheric exposure.

1.4.2 PITTING OR LOCALIZED CORROSION

Pitting may be defined as the most destructive, insidious and a limiting case of localised attack in which only small areas of the metal surface are attacked while remainder remains unaffected. The site of attack is determined by microscopic or submicroscopic features in passive fluids e.g. corrosion of stainless steel chromium and nickel in presence of ferric chloride and aluminium in presence of a neutral solution.

1.4.3 GALVANIC CORROSION

It is an accelerated electrochemical action due to the two different metals being in electrical contact and exposed to an electrolyte e.g. : – Heat exchanger failure in which aluminium tubes are supported by a perforated steel.

1.4.4 CREVICE CORROSION

It is characterised by the geometrical configurations of metal placed in contact with varying concentrations of solutions. Thus crevice corrosion can be called as concentration cell corrosion. The main examples of this type are rivetted plates, welded fabrications, threaded joints, contact of metal with nonmetal solids as plastic, rubber, sand etc. Force et al. have given the detailed description of crevice corrosion [4].

1.4.5 STRESS CORRSION

It is the spontaneous cracking resulting from the combined effect of prolonged stress and corrosive attack, for example the caustic embrittlement in boilers. Congleton and Yang have studied the stress corrosion cracking of sensitized type of 304 stainless steel [5].

1.4.6 EROSION - CORROSION

It is the acceleration in the rate of attack on a metal because of relative movement between a corrosive fluid and the metal surface resulting in the localised attack in the areas from where the film is removed. A detailed account of erosion - corrosion is given in the literature [6].

1.4.7 FRETTING CORROSION

It is the case of deterioration of metal resulting from the repetitive rubbing at the interface between two surfaces in corrosive environment for e.g. in aircraft engine parts. Various types of fretting corrosion and gear systems have been described by Lee [7].

1.4.8 FILIFORM CORROSION

It is characterised by the formation of a network of thread like filament of corrosion product on the metal surface coated with a transparent lacquer or paint film as a result of exposure to the humid atmosphere. A detailed account dealing with the factors and characteristics of filiform corrosion on architectural aluminium is described in the literature [8].

1.5 THEORIES OF CORROSION

1.5.1 HETEROGENOUS THEORY

According to this theory corrosion requires the presence of an impurity on metal thus creating a local cell set up between cathodic and anodic part of corroding surface. As a consequence of electrochemical reactions occurring at metal interface and ionically conducting moisture films or solution metal becomes unstable and thus corrosion occurs.

1.5.2 HOMOGENEOUS THEORY

According to wagner and Traud [9] metal unstability arises due to different electronic charge transfer reactions occurring simultaneously in opposite directions at metal / environment interface. For this, it is necessary that the potential difference

across the interface should be more positive than the equilibrium potential of the metal dissolution reaction and more negative than the equilibrium potential of the electronation reaction.

1.5.3 ELECTROCHEMICAL THEORY OF CORROSION

Though corrosion problem is as old as man's knowledge about the uses of metals but its mechanism was not known uptill eighteenth century. Wollaston [10] produced the first paper in 1801 regarding the mechanism of corrosion. The most acceptable electrochemical theory of corrosion was given by whitney [11] in 1903. Various other theories namely acid theory [12, 13] direct chemical attack theory [14], colloidal theory [15] have also been put forward but they are mainly restricted to specific systems. The electrochemical theory of corrosion is the only theory which is universally accepted and is applicable to the most of the corrosion processes.

Most of the corrosion reactions can be separated into two or more partial reactions which can further be divided into two classes, oxidation and reduction. An oxidation reaction is indicated by production of electrons as given below :–

$$M \rightleftharpoons M^{+} + e^{-} \quad \text{- - - - - - - - - - - - -} \quad (1)$$

This.reaction constitutes the basis of corrosion of metals. In a similar fashion, a reduction reaction is indicated by the consumption of electrons. For every oxidation reaction there must be a corresponding reduction reaction. In aqueous solutions, various reduction reactions are possible depending upon the system. Some examples of reduction reactions are given below : –

Hydrogen evolution :

$$2H^{+} + 2e^{-} \longrightarrow H_2 \quad \text{(in acidic system) - - - - - (2)}$$

Oxygen reduction :

$$O_2 + 4H^{+} + 4e^{-} \longrightarrow 2H_2O \quad \text{(in acid solution) - - - - - - - (3)}$$

$$O_2 + 2H_2O + 4e^{-} \longrightarrow 4OH^{-} \quad \text{(in netural and alkaline solution)}$$

Metal ion reduction :

$$M^{+n} + e^{-} \longrightarrow M^{+(n-1)} \quad \text{- - - - - - - - - - - - - - - - - (4)}$$

Metal deposition :

$$M^{+n} + n\,e^{-} \longrightarrow M \qquad \text{----------(5)}$$

The oxidation reactions are known as anodic reactions while reduction reactions are cathodic. During the corrosion more than one anodic and cathodic reactions may occur. Oxidation - reduction (redox) reactions can be understood by the example of corrosion of mild steel in sulphuric acid contaminated by ferric ions. Anodic reactions will occur as below : –

$$M \rightleftharpoons M^{+n} + n\,e^{-} \qquad \text{----------(5 a)}$$

All the component elements of mild steel (e.g. Fe, Mn, etc.) go into the solution as their respective ions. The electrons produced by these anodic (oxidation) reaction will be consumed by the cathodic (reduction) reactions. In this case, reaction (4) can be represented as below:

$$Fe^{3+} + e^{-} \longrightarrow Fe^{2+} \qquad \text{----------(6)}$$

Removing one of the availble cathodic reactions (e.g. removing reaction (6) by removal of the Fe^{+++} ions) will reduce the corrosion rate.

When a metal or alloy is immersed in a corrosive environment than there is a tendency of the metal / alloy to go into the solution (or dissolve). The production of ions and electrons builds a potential on the metal surface. This potential is called as electrode potential, it depends on (i) the nature of the metal (ii) the nature of the solution. It is calculated by the Nernst equation : –

$$E = E_0 + \frac{RT}{zf} \ln \frac{(Ox)}{(red)} \qquad \text{----------(7)}$$

where,

E_0 = Standard electrode potential

R = Gas constant (1.98 cal / gm equivalent)

F = Faraday constant (96,500 coulombs / gm equivalent)

T = Absolute temperature

Z = Number of the electrons transferred in the reaction

(Ox) = Concentration of oxidized species (mol / l)

(red) = Concentration of reduced species (mol / l)

The potential of a reaction is related to its free energy (ΔG) by:–

$$\Delta G = -z\,FE \qquad \text{----------(8)}$$

A negative value for the free energy corresponds a spontaneous reaction, whereas a positive value of Δ G indicates that the reaction has no tendency to proceed. The change in free energy accompanying an electrochemical or corrosion reaction can be calculated from a knowledge of the cell potential of the reaction.

It is the redox potential by which one can predict whether a metal will corrode in a given environment or not.

1.5.3.1 POTENTIAL- PH DIAGRAM

The use of oxidation reduction potential can be further extended by plotting these potentials as a function of solution pH. Such diagrams are called pourbaix diagram, [16] They are constructed using electrochemical calculations based on solubility data, equilibrium constants and the Nernst equation. The potential - pH diagrams for iron exposed to water is shown in Fig. 1.0. It is necessary to consider the following equilibria before drawing the pH - potential diagram for iron : –

$$Fe \rightleftharpoons Fe^{2+} + 2e^{-} \qquad \text{Corrosion Reaction---------(9)}$$

$$Fe \rightleftharpoons Fe^{3+} + 3e^{-} \qquad \text{Oxidation Reaction-------(10)}$$

$$2Fe^{2+} + 3H_2O \rightleftharpoons Fe_2O_3\downarrow + 6H^{+} + 6e^{-} \qquad \text{Precipitation Reaction----(11)}$$

$$Fe^{3+} + 2H_2O \rightleftharpoons Fe(OH)_2 + 2H^{+} \qquad \text{Hydrolysis Reaction------(12)}$$

$$2Fe^{+} + 3H_2O \rightleftharpoons Fe_2O_3 + 6H^{+} + 6e^{-} \qquad \text{Corrosion Reaction-------(13)}$$

$$Fe + 2H_2O \rightleftharpoons HFeO_2^{-} + 3H^{+} + 2e^{-} \qquad \text{Corrosion Reaction-------(14)}$$

$$HFeO_2^{-} + H_2O \rightleftharpoons Fe(OH)_3\downarrow + e^{-} \qquad \text{Precipitation Reaction----(15)}$$

$$Fe^{2+} + 2OH^{-} \rightleftharpoons Fe(OH)_2\downarrow \qquad \text{Precipitation Reaction----(16)}$$

Reactions (9), (10) and (15) are independent of pH and will be represented by

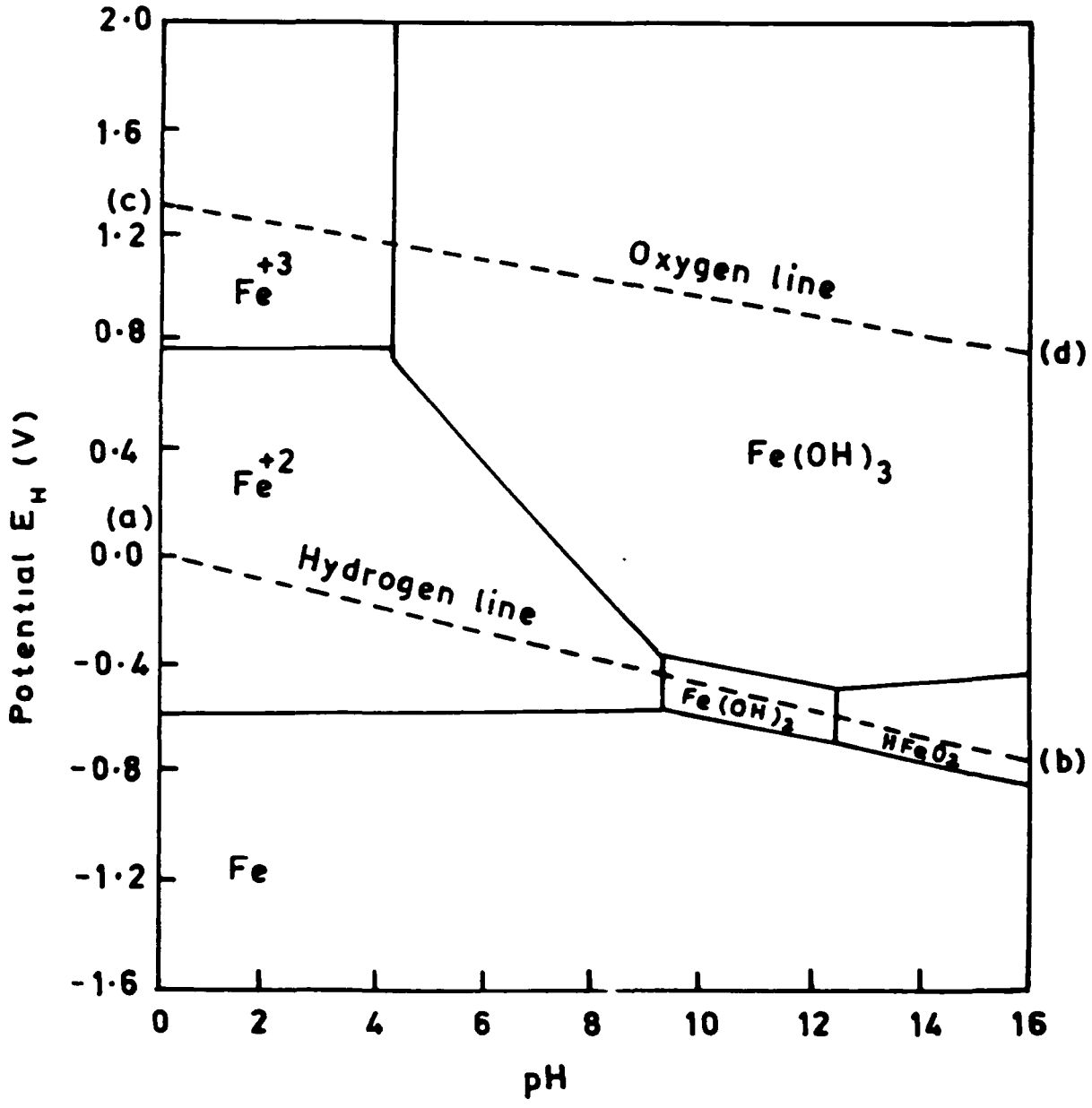


FIGURE 1.0 Simplified potential - pH diagram for Fe - H_2O system

straight horizontal lines, while reactions (11), (13) and (14) are dependent upon pH and potential and will be represented on the E_H / pH plots by sloping lines. Reaction (12) and (16) which only depend on pH will be represented by vertical lines. Oxygen is evolved above but not below line (cd) in accord with the reaction :–

$$H_2O \longrightarrow \tfrac{1}{2} O_2 + 2H^+ + 2e^- \quad \text{---------- (17)}$$

Hydrogen is evolved below but not above (ab) in accord with the reaction

$$H^+ \longrightarrow \tfrac{1}{2} H_2 - e^- \quad \text{---------- (18)}$$

As can be seen in Fig. 1.0, the redox potential of the hydrogen electrode (line "ab") lies above immunity region along all the pH scale. This means that Fe may be dissolved with evolution of hydrogen in aqueous solutions of all pH values. In the pH interval (9.4 - 12.5), however, a passivating layer of $Fe(OH)_2$ is formed (reaction (16). At higher pH values soluble hypoferrite can form with in a restricted active potential range. At a higher redox potential in the corroding medium, the passivating layer consists of $Fe(OH)_3$ or $Fe_2O_3 . n H_2O$ or Fe_2O_3 or Fe_3O_4 in different situations. Soluble ferrate (FeO_4^{-2}) can form in alkaline solutions at a very noble potential, but the stable field is not well defined.

The Pourbaix diagrams show at a glance specific conditions of potential and pH under which the immunity, corrosion or passivation may exist. Since the data on potential - pH diagram are thermodynamic, they convey no information about the rate of reactions.

The major uses of these diagram which can be constructed for all metals are as follows :–

(I) Predicting the conditions for prevention of corrosion

(II) Estimating the composition of corrosion products

(III) Predicting the environmental changes which will prevent or reduce corrosive attack.

1.6 CORROSION CONTROL METHODS

The corrosion reaction takes place at the metal / environment interface, so corrosion can be controlled by :–

1. Modifying the composition of metal.
2. Modifying the metal surface
3. Altering the metal / environment potential

The account of various methods controlling corrosion is given in the literature [17]. The general classification of various corrosion control methods is summarised in Table 1.0.

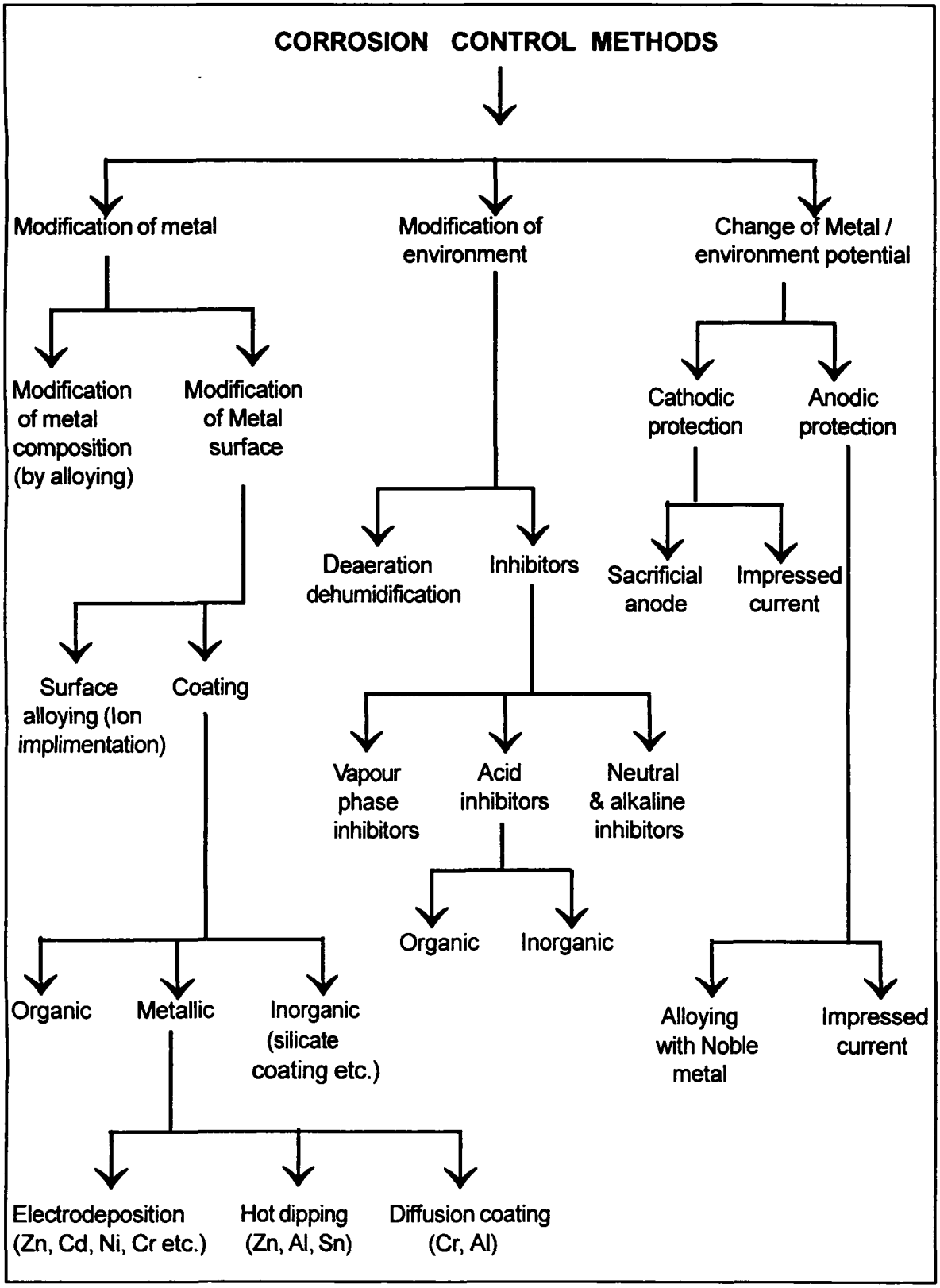
1.7 CORROSION CONTROL BY THE APPLICATION OF INHIBITORS

An inhibitor is a chemical substance which when added in a small concentration to the corrosive environment causes a substantial reduction in the rate of corrosion of metal either by reducing the probability of its occurrence (deterrent) or by reducing the rate of attack (retardant) or by both. Inhibitors are very specific to the medium for which they are used.

According to NACE, Inhibitor is a substance which retards corrosion when added to an environment in small concentration [18] and the recent ISO definition of an inhibitor is a chemical substance which decreases the corrosion rate when present in the corrosion system at a suitable concentration without significantly changing the concentration of corrosive medium [19]. Inhibitors may also be defined on electrochemical basis as substances that reduce the rates of either or both partial anodic oxidation and cathodic reduction reaction.

In the majority of cases inhibition is achieved through interaction or reaction between the corrosion inhibitor and metal surface, resulting in the formation of an inhibitive surface film, this may occur directly at the metal / environment interface or via precipitation. In other cases the chemistry of the environment may be modified to render it less corrosive, e.g. by chemically scavenging dissolved oxygen, chemically neutralising dissolved acidic gases, adjusting pH to promote stable (inherent) passivation

Table -1.0 Methods of corrosion control



1.8 CLASSIFICATION OF INHIBITORS

Classification of corrosion inhibitors is some what a subjective exercise being very much dependent on the method employed. For example one could choose the inhibitors to classify them in terms of mechanism, environment to which they are added, metal to be protected or inhibitor chemistry, of which none are mutually exclusive. Some of the main classifications used particularly for inhibitors are as follows :–

1. 'Safe' or 'dangerous' inhibitors
2. 'Oxidizing' or 'non-oxidizing' inhibitors
3. Acid or alkaline and neutral inhibitors
4. Vapour phase inhibitors
5. Anodic or cathodic or mixed inhibitors

According to Putilova [20] inhibitors are of three types:-

Type A	forms a protective film on the metal surface
Type B	reduces the aggressiveness of the corrosive media
Type AB	forms a protective film and also reduces the aggressiveness of the corrosive agent

1.8.1 SAFE OR DANGEROUS INHIBITORS

This classification relates to the type of corrosion that will occur when the concentration is below the minimum or critical value.

Thus when any inhibitor present in insufficient amount, it allows only a uniform type of corrosion to proceed at a rate not greater than that obtaining in an uninhibited system, is called ' safe' inhibitor such as carbonates, zinc sulphates do not interfere with anodic reaction but inhibit cathodic reaction, whereas ' dangerous' inhibitor leads to enhance the localised attack e.g. pitting when present in below critical concentration, such as some chromates, nitrates, phosphates, molybdates, tungstate etc.

1.8.2 OXIDIZING OR NON OXIDIZING INHIBITORS

These are characterised by their ability to passivate the metal. In general non-oxidizing inhibitor require the presence of dissolved oxygen in the liquid phase

for the maintenance of the passive oxide film for e.g. phosphate and molybdate, whereas dissolved oxygen is not necessary with oxidizing inhibitor for e.g. nitrates and nitrites work as anodic oxidizing passivators.

1.8.3 ACID INHIBITORS

This may be further classified in to inorganic and organic inhibitor

(I) INORGANIC INHIBITORS

In strong acid solutions, Br^-, I^- have been found to be effective inhibitors [21]. The oxides like As_2O_3, Sb_2O_3 have been reported as the inhibitors in acid media. These substances get deposited in the form of metal on iron surface and increase the hydrogen overvoltage and subsequently reducing the corrosion [22]. Addition of heavy metal ions such as Pb^{+2}, Mn^{+2} and Cd^{+2} inhibit the corrosion of iron in acids.

This effect is due to the under potential deposition of metal ions, which leads to complete coverage of metal adsorbate on the iron surface [23]. Antimony chloride dissolved in concentrated hydrochloric acid is used in the laboratory for stripping deposits of zinc, cadmium, tin and chromium from steel and with the addition of stannous chloride for removing scale and rust.

(II) ORGANIC INHIBITORS

Various classes of organic compounds such as alcohols, amines, aldehydes, mercaptans, alkaloids, anisidines, aliphatic, aromatic, heterocyclics, fatty acids, polymers, natural products etc., and some condensation products have been extensively used as corrosion inhibitors in the recent past years. The effectiveness of a large number of organic compounds as inhibitors have been correlated [24-27] to different factors like chemical structure, substituent effect, steric effect, Hammett constant, molecular weight carbon chain length, basicity (pKa), dipole moment, magnetic susceptibility, pH of the solution, temperature, nature of metal, velocity of liquid flow and NMR shift etc. Schmitt [28] has reviewed the application of inhibitors for acid medium. The study of various organic compounds in relation to their different aspects of inhibitors in different environments has been excellently reviewed by Sanyal [29].

An organic compound can be cathodic, anodic or both depending on its reaction

at the metal surface and how the potential of the metal is affected [30]. Generally cathodic inhibitors increase cathodic polarization and shift the corrosion potential to more negative values and anodic inhibitors enhance anodic polarization and shift the corrosion potential to more positive values.

1.8.4 ALKALINE AND NEUTRAL INHIBITORS

These inhibitors include cathodic inhibitors, those which increase the cathodic polarization, anodic inhibitors (passivating inhibitors) which enhance the anodic polarization and mixed or general inhibitors which act as both cathodic and anodic inhibitors.

Anodic inhibitors form an oxide or some other insoluble film.Insufficient concentration of anodic inhibitors will lead to severe pitting. Sodium chromate is one of the most widely used and efficient inhibitor. Sodium silicate is generally used in hot water systems. The other compound used in natural and alkaline media are borates, molybdates and salts of organic acids like benzoates and salicylates.

1.8.5 VAPOUR PHASE INHIBITORS

The substances which protect metallic materials against atmospheric corrosion are called vapour phase inhibitors. They are also called as volatile corrosion inhibitors. These are used in boilers to prevent corrosion in condenser tubes by neutralising the acidic CO_2. They are transported to the site of corrosion in a closed system by volatilization from a source compounds of this type inhibit corrosion by making the environment alkaline.

Volatile solids such as nitrates and benzoates salts of dicyclohexyl amine and cyclohexyl amines are used in closed vapour spaces like shipping containers. The inhibitor vapour condenses on contacting a metal surface and is hydrolysed by moisture present to liberate nitrite and benzoate ions which in the presence of available oxygen are capable of passivating steels as they do in aqueous solution [31].

1.8.6 ANODIC INHIBITORS

Those substances which reduce the anode area by acting on the anodic sites

and polarise the anodic reactions are called anodic inhibitors. In the presence of anodic inhibitors, displacement in corrosion potential (E_{corr}) takes place in positive direction. They suppress corrosion current (I_{corr}) and reduce the corrosion rate. In aqueous acid media, the corrosion of metals takes place at the anodic area through metal dissolution. The cathodic reaction generally involves the reduction of hydrogen ions or by oxygen reduction to hydroxyl ions. These reactions may be represented schematically as shown in Fig.1.1a. The curve E_{corr} A represents the anodic reaction while E_{corr}C represents the cathodic reaction and the point B where both the anodic and cathodic reactions intersect corresponds to corrosion potential (E_{corr}) and corrosion current (I_{corr}). The substances which retard the anodic reaction lead to the enhancement of anodic polarization. In this situation, anodic curve becomes E^a_{corr} A (Fig.1.1a) and the current I^a_{corr} corresponding to 0 is less than I_{corr} (corrosion current) in absence of the inhibitors and the rate of corrosion is decreased. Anodic inhibitors which cause a large shift in the corrosion potential are called passivating inhibitors, if used in insufficient concentrations, they cause pitting and sometimes an increase in corrosion rate. The anodic inhibitors are frequently used because they are very effective in sufficient quantities. Anodic inhibitors cause passivity by increasing up the corrosion reaction to the extent that the anodes are polarised to a passive potential. If corrosion of a metal or alloy is controlled by the anodic reaction (anodic control), it is obvious that decrease in overall corrosion should be proportional to the portion of the anodic areas being polarised. On the other hand, if corrosion is controlled by the cathodic reactions (cathodic control), the corrosion current and therefore the total amount of the corrosion is not affected by decreasing the anodic areas. In this case, the same amount of corrosion must be distributed over a smaller anodic area, resulting in intensified localised attack (pitting type of corrosion).

The inhibition mechanism of the anodic corrosion inhibitors has been a matter of long dispute and there have been two points of view advanced to explain their action. One supports the formation of protective insoluble film on metals in the presence of the inhibitors while, the other can be understood in such a way that, the inhibitors get adsorbed by specific force interaction or through chemisorption on the surface of metals.

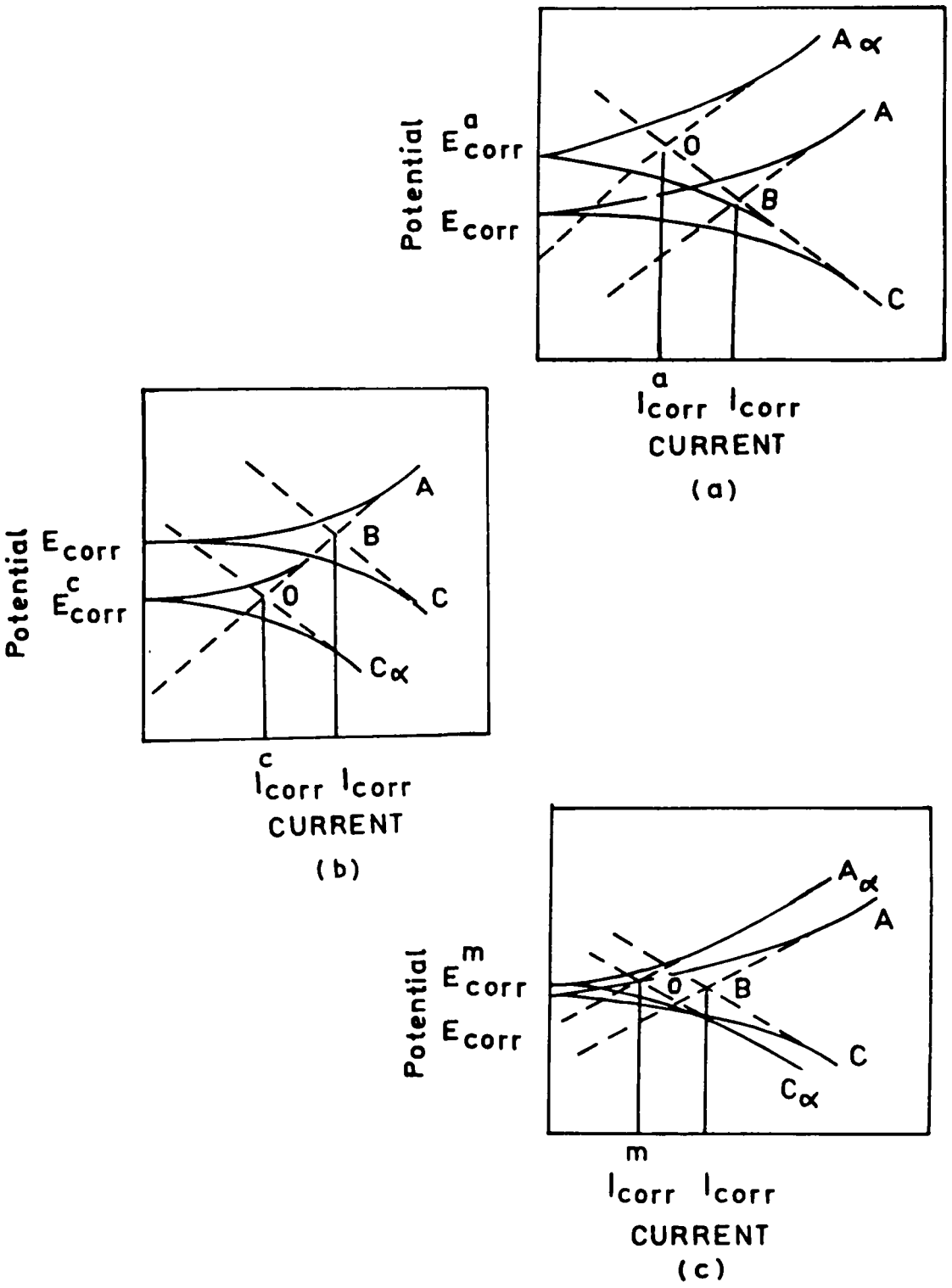


FIGURE 1.1 Mechanism of action of corrosion inhibitors based on polarization effects

(I) PROTECTIVE FILM MECHANISM

It has been observed that the anions present in potassium and sodium salts act as anodic inhibitors by forming a sparingly soluble salt with the metal. Hoar and Evans [32] have shown that chromates react with ferrous ions and precipitate an adherent protective film of hydrated ferric and chromic oxides on the anodic areas. It has been shown that during the inhibition of corrosion by sodium hydroxide [33], orthrophosphate [34], nitrite [35], chromate [36] and other anodic inhibitors like sodium carbonate, acetate, benzoate and molybdate [37] in aerated solutions, there occurs the formation of an invisible protective thin film by γ - Fe_2O_3.

(II) ADSORPTION MECHANISM

According to Uhling [38] for inhibition oxide film formation is not necessary, primary inhibition by chromates and other oxidizing inhibitors is due to physical and activated adsorption - chemisorption, through which valence forces of the surface metal atoms are satisfied. These views were confirmed from the measurements of electrode potential as well as the measurement of residual activity of an iron sample immersed in radioactive chromate solution and subsequently washed thoroughly with distilled water [39 - 40]. Later on, it was found that anions adsorbed at the oxide solution interface were responsible for inhibition rather than the formation of metal oxide film [41].

1.8.7 CATHODIC INHIBITORS

Those inhibitors which reduce the cathode area by acting on the cathodic sites and polarize the cathodic reactions are called cathodic inhibitors. They displace the corrosion potential in the negative direction (E^c_{corr}) and reduce corrosion current, thereby retard cathodic reaction and suppress the corrosion rate (Fig.1.1b). In this situation, the point of intersection is at 0 and corresponding current I^c_{corr} will be lower than that without inhibitor (I_{corr}).

The cathodic inhibitors, with a few exceptions [42] do not lead to intensified or localised attack since cathodic areas are not attacked during corrosion. If corrosion is controlled by cathodic reactions, the added cathodic inhibitor would decrease the cathodic area and hence over all corrosion rate. On the other hand, if the corrosion

is controlled by anodic reaction, decrease in cathodic area would increase cathodic current density but will have no effect on the nature of corrosion. The increase in cathodic current density may cause the reduction of substances present which would not otherwise be reduced. Mann et. al. [43 - 45] and other investigators [46 - 49], working on numerous organic inhibitors in acid media have proposed that inhibitors exist in onium structure and get adsorbed on the cathodic areas of the surface by force of physical adsorption, and chemisorption. In contrast, Bockris and Conway [50] have claimed that the action of cathodic inhibitors is due to an increase of the hydrogen overvoltage rather than by an adsorbed inhibitor film on the metal surface. The cathodic inhibition is due to the general adsorption of the inhibitors on the metal surface, however remains the most accepted theory [51, 52]

Cerium was used instead of Chromium compounds as cathodic inhibitor for aluminium - copper alloys in chloride containing solutions. Electrochemical studies has shown that cerium inhibits corrosion by reducing the rate of cathodic reaction [53].

Like anodic inhibitors, cathodic inhibitors are not dangerous but safe, when present in solution in insufficient quantities and involve no additional risk of pitting attack.

1.8.8 MIXED INHIBITORS

There are number of chemicals which inhibit the metallic corrosion by interfering with both the cathodic and anodic reactions are called mixed inhibitors. This type of inhibition can be represented by Fig. (1.1.c). The anodic and cathodic reactions are represented by $E^{m}_{corr}A$ and $E^{m}_{corr}C$ respectively and corrosion current I^{m}_{corr} in presence of such type of inhibitors is considerably less than that in their absence. Glue, gelatin and other high molecular weight substances fall in this category. It is believed that the action of such type of inhibitors at the metal - liquid interface is due to their concentration or coagulation providing a shield to the metal surface. Machu [54 - 55] claims that their action is mainly due to the formation of porous layer which increases the electrical resistance of the surface layer.

1.9 RECENT CLASSIFICATION OF INHIBITORS

A recent classification [56] on the basis of the mechanism of inhibitive action, has divided the corrosion inhibitors into four major categories (Table 1.1):–

(I) Barrier layer formers

(II) Neutralizers

(III) Scavengers

(IV) Miscellaneous

(I) BARRIER LAYER FORMERS

These materials form barrier layers on the corroding metal surface and reduce the corrosion rate. This type is the most important and forms the largest category of corrosion inhibitors. The barrier formers have been further classified into oxiders, adsorbed layer formers and conversion layer formers. In general, these inhibitors are effective in reducing both the cathodic and anodic reaction rate except for the oxidizing inhibitors which shift the corrosion potential of the metal to more positive value at which a stable oxide or hydroxide is formed and protects the metal surface.

(II) NEUTRALIZERS

The neutralizing inhibitors remove the hydrogen ions from the corrosive environment and hence the concentration of the cathodic reactant. These inhibitors are used in the treatment of boiler waters, oil field applications and also in ethylene glycol cooling systems.

(III) SCAVENGERS

These are similar to neutralizers but used to remove corrosive species other than hydrogen ions. Typical example of scavenger system is the use of hydrazine in boiler system to remove the traces of oxygen which is a cathodic reactant.

(IV) MISCELLANEOUS

These inhibitors include materials such as scale inhibitors and biological growth inhibitors which reduce corrosion by interfering with other processes.

The above classification of inhibitor types by function appears to give a fairly

TABLE 1.1 Recent Classification of inhibitors

TYPE	EXAMPLE
(I) Barrier layer formers	
A. Adsorbed layer formers	Acetylenic alcohol in HCl
1. Cathodic inhibitors	
2. Anodic inhibitors	
3. Mixed inhibitors	
B. Oxidizing inhibitors-	
Passivators	$NaNO_2$ in water
C. Conversion layer formers	
1. Insoluble Corrosion products	Phosphate
2. Cathodic deposits	$CaCO_3$
(II) Neutralizing inhibitors	
1. Volatile	Cyclohexylamine in boilers
2. Non - Volatile	Amines, brine
(III) Scavengers	
1. Oxygen Scavengers	Na_2SO_3 in boilers
2. Decomposition inhibitors	Dioxane in CH_3CCl_3
(IV) Miscellaneous	
1. Biological growth inhibitors	Quaternary amines
2. Scale inhibitors	Phosphate

simple and concise approach, although it has limitations in cases where the mechanism is not known. In general the use of neutralizing and scavenging type inhibitors seems to be the best suited for closed systems where such chemicals are not lost in the systems. In open systems however the use of inhibitors is difficult to justify.

1.10 MECHANISM OF INHIBITION IN ACIDS

The inhibitive action of organic compounds occurs on the metallic surface due to interaction between the inhibitor and the metal surface by adsorption phenomenon. In this process the molecules are held on to the surface of the adsorbent by valence forces i.e., variation in the charge of the adsorbed substances and a transfer of charge from one phase to the other. Therefore, the molecular structure of the inhibitors assumes special significance [57]. The electron density at atoms of functional group constituting a reaction centre affects the strength of the adsorption bond, it also depends on the properties of the metal, as well as on the polarizability of the functional group [58, 59]. Inhibition can be explained by LFER correlation [60, 61].

1.10.1 FACTORS AFFECTING ADSORPTION MECHANISMS

(I) SURFACE CHARGE ON THE METAL

The magnitude and sign of the surface charge of the metal play a very important role for the establishment of the adsorption bond. The effects exercised by organic inhibitors on the electrode reactions must be connected with the modifications induced in the structure of the electrochemical double layer because of their adsorption. In solution the charge on a metal can be expressed by its potential with respect to the zero charge potential. This potential, often referred to as the ø potential, is more important than the potential on a hydrogen scale and sign of these two potentials are different [62]. As the potential becomes more positive, the adsorption of anions is favoured and as the potential becomes more negative, the adsorption of cation is favoured.

(II) REACTION OF ADSORBED INHIBITORS

In some cases, the adsorbed corrosion inhibitors may react to form a product

by electrochemical reduction, which may also be inhibitive in nature. Inhibition due to the added substances has been termed as the primary inhibition and that due to the reaction product as the secondary inhibition [63]. In such cases, the inhibitive efficiency may increase or decrease with time according to whether the secondary inhibition is more or less effective than the primary inhibition [64].

(III) INTERACTION OF ADSORBED INHIBITOR SPECIES

The lateral interactions between adsorbed inhibitor species becomes significant with increase of surface coverage of the adsorbed species. This lateral interaction may be either attractive or repulsive. Attractive interaction occurs between molecules containing large hydrocarbon components. The repulsive interactions occur between ions or molecules containing dipoles and lead to weaker adsorption at high coverage [65].

(IV) INTERACTION OF THE INHIBITOR WITH WATER MOLECULES

The surfaces of metals in aqueous solution are covered with adsorbed water molecules. Adsorption of inhibitors takes place by the displacement of adsorbed water molecules from the surface, which involves free energy for adsorption. It is found to increase with the energy of solvation of the adsorbing species [66].

(V) STRUCTURE OF INHIBITORS AND THEIR ADSORPTION

The inhibitors can bond to metal surfaces by electron transfer to the metal thus forming adsorption bond. Generally the inhibitors are the electron donor and the metal is the electron acceptor. The strength of this bond depends on the characteristics of both the adsorbate and adsorbent. The electron transfer from the adsorbed species is favoured by the presence of relatively loosely bound electrons, such as may be found in anions and neutral organic molecules containing lone pair electrons or π electron systems associated with multiple bonds or aromatic rings.

Most of the organic compounds have at least one polar atom, i.e. nitrogen, sulphur, oxygen and in some cases selenium and phosphorous. In general, the polar atom is regarded as the reaction centre for the establishment of the chemisorption process. In such cases, the adsorption bond strength is determined by the electron density of the atom acting as the reaction centre and by the polarizability of the polar

atoms. The effectiveness of the polar atoms with respect to the adsorption process varies in the following sequences : –

Selenium > Sulphur > Nitrogen > Oxygen

The idea of electron density acquires particular importance in aromatic or heterocyclic inhibitors whose structure may be affected by the introduction of substituents in different positions of the rings. The availability of electron pairs for the formation of chemisorption bond can thus be altered by regular and systematic variations of the molecular structure.

1.10.2 INFLUENCE OF INHIBITOR ON CORROSION REACTION

An inhibitor may decrease the rate of anodic process, the cathodic process or of both processes. The change in corrosion potential on the addition of the inhibitor is the indication of a retarded process [67]. A shift of the corrosion potential in the positive direction indicates mainly retardation of the anodic process (anodic control) whereas shift in the negative direction indicates the retardation of the cathodic process (cathodic control). Little change in the corrosion potential suggests that both anodic and cathodic processes are retarded.

In the presence of an inhibitor, a shift of polarization curves without a change in the Tafel slope indicates that the adsorbed inhibitor acts by blocking active sites so that reaction can not occur rather than affecting the mechanism of the reaction [68]. A change in the Tafel slope is the indication of affecting the mechanism of the reaction. Inhibitors in acid solutions affect the corrosion reactions of metals in the following way :–

(I) FORMATION OF A DIFFUSION BARRIER

The adsorbed inhibitors which form a surface film on the metal surface, can act as a physical barrier to restrict the diffusion of ions or molecules to or from the metal surface and so retards the corrosion reactions. This type of behaviour occurs in the inhibitor containing large molecules [69].

(II) BLOCKING OF REACTION SITES

The inhibitors may adsorb on the metal surface to prevent the surface metal atoms from participating in either the anodic or cathodic reactions of corrosion. This

blocking process reduces the surface metal atoms at which these reactions can occur and hence the rates of these reactions. The mechanism of the reactions are not affected and the Tafel slopes of the polarization curves remain unchanged. Adsorption of inhibitors at low surface coverage tends to occur at anodic sites, causing retardation of the anodic reaction. At high surface coverage, adsorption occurs on both anodic and cathodic sites, and both reactions are inhibited.

(III) PARTICIPATION IN THE ELECTRODE REACTIONS

The electrode reactions involve the formation of adsorbed intermediate species with surface metal atoms. The presence of adsorbed inhibitors will interfere with the adsorbed intermediate but the electrode processes may then proceed by alternative paths through intermediates containing the inhibitor. In these processes, the inhibitor affects the reaction and the inhibitor remain unchanged with a change in the Tafel slope [70]. Inhibitors may retard the rate of hydrogen evolution on metals by affecting the mechanism of the reaction with the increase in Tafel slopes of cathodic polarization curves. This effect has been observed on iron in the presence of inhibitors such as phenyl thiourea [71].

(IV) ALTERATION OF THE ELECTRICAL DOUBLE LAYER

The adsorption of ions or species which can form ions on metal surfaces will change the electrical double layer at the metal solution interface, and this in turn will affect the rates of the electrochemical reactions.

1.11 ADSORPTION ISOTHERMS

An adsorption isotherm gives the relationship between the coverage of an interface with an adsorbed species (the amount adsorbed) and the concentration of the species in solution [72]. Various adsorption isotherms have been formulated.

Table 1.2 gives the list of isotherms and their corresponding equations [73]. Interpretation of the inhibition characteristics of organic molecules can be made by fitting the data to one of the adsorption isotherms.

It was shown by Foley [74] that tetraisoamyl ammonium sulphate has little influence on the dissolution of iron in 4N sulphuric acid. However when 0.005N KI was added, the organic cation is adsorbed reducing the double layer capacity and the dissolution of iron is very much decreased.

The inhibition efficiency of acetylenic compounds has been greatly improved when combined with amines or thio compounds [75]. Halide ions are known both to stimulate and inhibit the corrosion of metals [76]. The synergistic effect takes place due to co - adsorption of ions on the metal surface [77].

1.13 CORROSION INHIBITION MONITORING TECHNIQUES

The various techniques employed for corrosion monitoring have been classified as:–

a. Non electrochemical methods

b. Electrochemical methods.

The measurement of corrosion rates in the presence of corrosion inhibitors by weight loss and electrochemical methods have been reviewed by Mercer [78].

1.13.1 NON ELECTROCHEMICAL METHODS

These include techniques like weight loss measurement and gasometric methods. The main disadvantage of these methods is that these require relatively long exposure times of the corroding systems. Also the chemical methods are in general restricted to systems which do not form adherent layers of corrosion products.

(I) WEIGHT LOSS MEASUREMENTS

This method is the most reliable method. The electrochemical measurement results are usually compared with weight loss data. Here the change in weight of the specimen is determined by immersing the specimen in the corrosive medium for a fixed time. The weight loss is usually expressed in mils per year (mpy) or milligrams per square decimeter per day (mdd).

EXPRESSIONS OF CORROSION RATE

Corrosion rates have been expressed in a variety of ways in the literature. The following are the major systems of corrosion units.

i. ipy .... inches per year

ii. mpy .... mils per year

(1 mil = 0.001 inch = 25.4 µm = 0.0254 mm)

iii. mmy .... milli mils per year

iv. ipmo .... inches per months

v. mdd .... milligrams per square decimeter per day

Usually corrosion rates are expressed in two basic units mpy and mdd. The corrosion rates in mpy and mdd scales can be directly calculated from the following expressions :-

$$\text{(I)} \quad \text{mpy} = \frac{w \times 534}{a \times t \times d}$$

where

w = the weight loss in grams

a = the area of the specimen in square inches

d = the density of the specimen in gram / cm^3

t = the time in hours

If the area is calculated in square centimetres then the expression for mpy is:–

$$\text{(II)} \quad \text{mpy} = \frac{82.75 \times w}{a \times t \times d}$$

$$\text{(III)} \quad \text{mdd} = \frac{53.5 \times w}{a \times t}$$

where, **w** = the weight loss in grams

t = the time in hours

a = the area in square centimeters.

All the other expressions can be calculated from these two basic units for corrosion rates, using the conversion table.

$$\text{mpy} = 1000 \text{ X ipy} = 12100 \text{ X ipmo} = \frac{1.44}{d} \text{ X mdd}$$

It can be mentioned here that in general corrosion rate of less than 5 mpy indicates satisfactory service behaviour, 5 - 50 mpy moderate to fair corrosion resistance and corrosion rates above 50 mpy would be unsatisfactory for service.

The computerized system *SOFTCOR - DC - PHTS* program is developed to deal with the problems of monitoring the corrosion rates of metals in acid media and to process the experimental data without the intervention of an operator [79].

(II) GASOMETRIC METHODS

This method yields reliable and accurate results with a high degree of reproducibility. In this method the volume of hydrogen gas (in acid corrosion) evolved during a corrosion reaction is directly measured at a constant temperature. The corresponding metal loss can be calculated. This technique has been used for the inhibitor studies by Nathan [80] and Hackerman [81]. Mathur et. al. [82] have designed a gasometric unit with which corrosion rates could be monitored under control conditions of temperature and pressure without any aqueous tension correction. Also this technique has been successfully applied for the determination of corrosion kinetics parameters by them.

However this technique has certain limitations such as it can not be applied to a strong oxidizing medium like nitric acid, to systems where the inhibitor used undergoes reduction with the hydrogen gas evolved etc.

1.13.2 ELECTROCHEMICAL METHODS

The electrochemical methods are most widely used for the study of inhibitors.

(I) POLARIZATION METHODS

In this method the behaviour of inhibitor is understood by drawing a Tafel plot Fig. 1.2 in absence and presence of inhibitor.

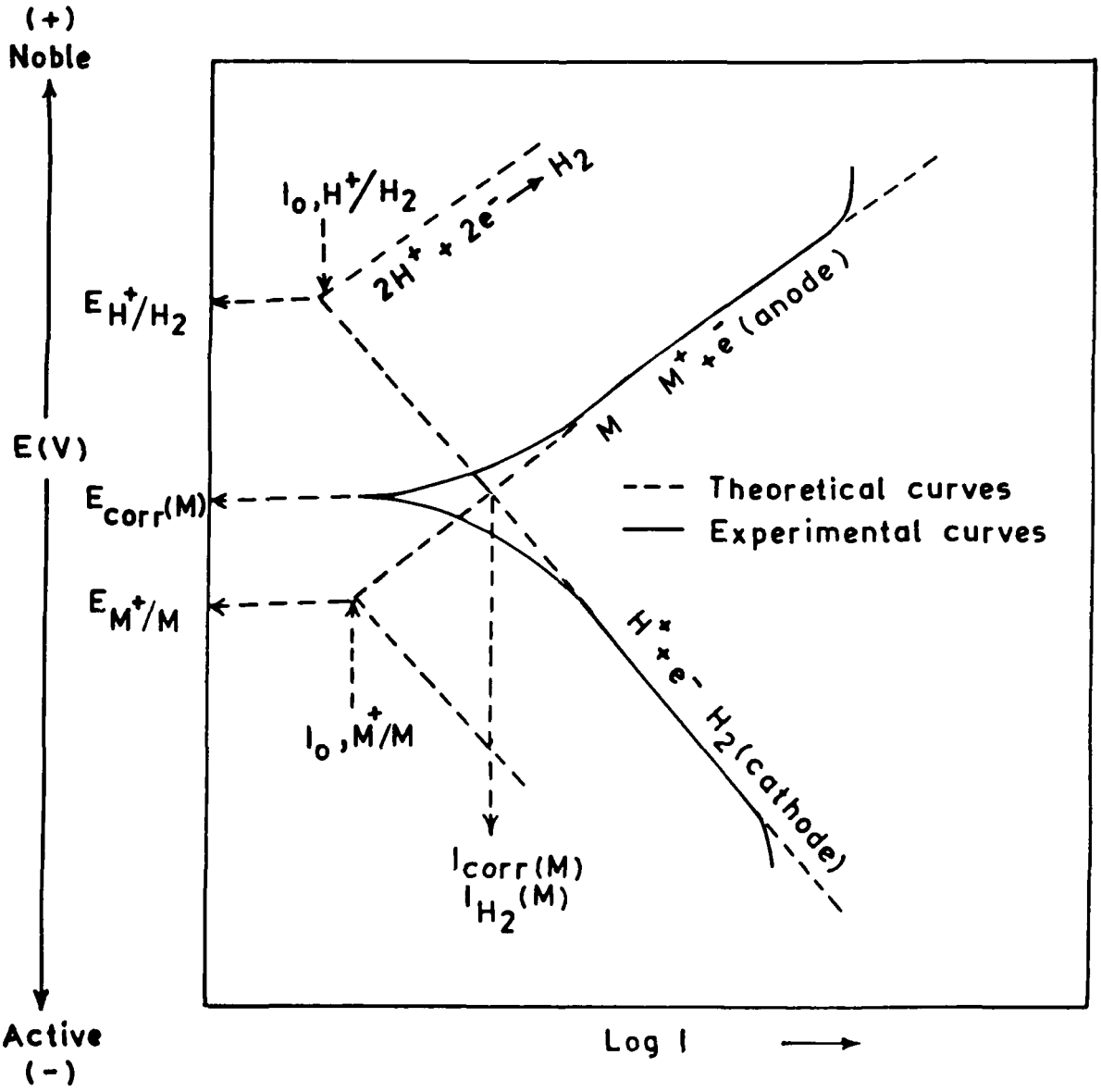


FIGURE 1.2 Polarization curves for a corroding electrode
E_{corr} = Corrosion potential
I_{corr} = Corrosion current

The percentage inhibition is calculated from the formula : –

$$I\ E\ (\%) = \frac{I_{o\ corr} - I_{corr}}{I_{o\ corr}}$$

I_{ocorr} = Corrosion current density (Corrosion rate) in absence of inhibitor.

I_{corr} = Corrosion current density (Corrosion rate) in presence of inhibitor.

The corrosion rate is determined from the polarization data in two ways :-

(a) Tafel extrapolation method

(b) Linear polarization method

In Tafel extrapolation method the linear portion of the Tafel curve is extrapolated. The point of intersection is referred to as I_{corr}.

Linear polarization method, provides the value of absolute corrosion rate from the following relation.

$$I_{corr} = \frac{\beta_a \cdot \beta_c}{2.3\ (\beta_a + \beta_{c)}} \times \frac{1}{R_p}$$

where β_a and β_c are Tafel constants,

$1/R_p = \Delta i / \Delta E$ = polarization resistance.

(II) IMPEDANCE METHOD

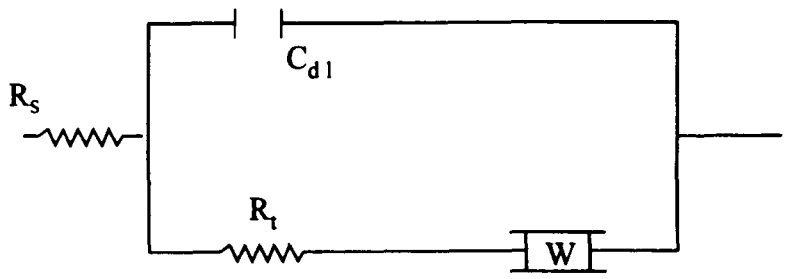
The impedance technique [83 - 88] has become a popular tool for the measurement of corrosion rate in recent years. A recent publication describes the recent advancements on EIS techniques [89]. The main advantages of this method are:-

(I). Applicable to low conductivity systems

(II). Provides mechanistic information

(III). Solution resistance is completely eliminated.

The electrical equivalent circuit for the corroding system is given below :-



R_S = Solution resistance

R_t = Charge transfer resistance

W = Warburg impedance

C_{dl} = Double layer capacity

The inhibition efficiency of the inhibitor can be determined from AC impedance method [90, 91] by the following formula : –

$$IE\ (\%) = \frac{1/R_{to} - 1/R_t}{1/R_{to}} \times 100$$

Where, R_t and R_{to} are the charge transfer resistance with and without inhibitor. For determination of R_t very small potential is applied as a function of frequency (usually 60 KHz - 1mHz). The impedance of the corroding system for various frequencies can be measured using lock - in - amplifier. A plot of z (real) vs z" (imaginary) for various frequencies gives a semicircle (Nyquist) plot which cuts the real axis at higher and lower frequencies. At higher frequency it corresponds to R_S and at lower frequency it corresponds to $(R_S + R_t)$. The difference between the two values gives R_t. From R_t the corrosion current can be calculated using Stern-Geary equation: –

$$I_{corr} = \frac{\beta_a \cdot \beta_c}{2.3\,(\beta_a + \beta_c)} \times \frac{1}{R_t}$$

The double layer capacitance can be determined from the frequency at which Z" is maximum from the relation.

$$F_{z'' max} = \frac{1}{2\pi C_{dl} \cdot R_t}$$

1.14 OTHER METHODS

The methods such as Radio tracer technique, Spectroscopic method, X - ray photoelectron spectroscopy, Auger electron spectroscopy, Ellipsometry, Hydrogen permeation have also been used for studying the inhibition phenomenon.

1.14.1 RADIO TRACER TECHNIQUE

A better knowledge of inhibition phenomena can be obtained by Radio Tracer method [92] with labelled inhibitor. It is possible to detect traces of substance adsorbed even under extreme dilution.The method consists of bringing about the adsorption of compound under examination on the metal (electrode) by putting the electrode in the electrolyte containing the radio active organic substances. The electrode is taken out and washed. It is subjected to a count determination to measure the activity. It is compared with a standard and the amount of substance adsorbed is found.The decrease in the concentration of the labelled additive in the solution as a result of adsorption can also be measured. Bockris [93] developed a special type of cell which permits the study of adsorption under definite conditions of applied potential.

1.14.2. SPECTROSCOPIC TECHNIQUE

The results of I. R and U.V spectra of the adsorbed products are very useful in the interpretation of inhibition phenomena. I.R. studies help to predict the functions of the adsorption bonds and on the arrangement of the inhibitor molecules on the surface of the metal. Schwabe [94] showed from I. R. studies that in the case of corrosion inhibition with dibenzylsulfoxide, the product adsorbed on the electrode was dibenzylsulphide. U.V. spectroscopy has been used to determine the amounts of inhibitor adsorbed on the electrode by evaluating the decrease in solution concentration under condition of free corrosion [95]. Suetaka [96] developed a

technique to determine directly the amount of inhibitor adsorbed by spectra recorded on metallic electrodes. Riggs et. al. [97] obtained NMR spectra of aniline and substituted anilines. They have observed a good correlation between chemical shift and coefficient of inhibition of steel corrosion.

X - ray, Electron diffraction and Ellipsometric techniques [98] have been employed to study the films formed on the metal surface by the inhibitors. Surface enhanced Raman spectroscopy has been used to investigate the mechanism of adsorption of Octadecyldimethylbenzylammonium chloride, an aromatic amine on carbon steels [99, 100].

1.14.3 AUGER ELECTRON SPECTROSCOPY (AES)

In Auger Electron Spectroscopy [101, 102], a specimen is excited with an electron beam causing inner shell electrons to be removed from the atoms present. The outer shell electrons fill the created vacancies through a relaxation mechanism and so called "Auger electrons " are ejected from the material. An "Auger spectrum " is obtained by plotting the derivative of the electron energy distribution versus energy. The typical depth analysis with AES is of the order of 10 Å or less and elemental concentrations as low as 0. 1% of monolayer can be detected and identified. Both qualitative and quantitative information can be obtained for all elements above helium. The inner core vacancy is created by electron bombardment of the surface with electrons having energies in the range of 1 - 5 kev. Auger electrons are generated having energies in the range 0 to 2000 ev and only those electrons coming from within few monolayers of the surface escape with characteristic energy. The depth profiles of the surface films are obtained by sputtering the surface very slowly by Ar^+ ions. The absolute thickness of the surface film cannot be determined but the information about the thickness relative to the sputtering of Ta_2O_5 can be easily obtained.

1.14.4 POLAROGRAPHIC TECHNIQUE

The polarographic method is employed for the study of corrosion and has the practical utility in the detection of minute changes in the corrosive system. In this method, the potential is gradually increased in the direction of reducing the substance

present in aqueous solutions. At the reduction potential of the substance, the current suddenly increases. The height of the peak in the current versus time curve indicates the concentration of the substance present.

1.14.5 ELECTROCAPILLARY TECHNIQUE

The electrocapillarity technique is one of the newest update methods introduced for the study of corrosion inhibitors [103, 104]. It consists of measuring the interfacial tension of the electrode / electrolyte interface as a function of applied potential. The shift of electro - capillary curve, i.e. potential and surface tension curve, in the negative region after the addition of the inhibitor shows that adsorbed species are anionic in nature. In the presence of cationic type of inhibitors, the curve shifts towards anodic potential

1.14.6 NUCLEAR MAGNETIC RESONANCE

This method has been applied to study the electronic structure of organic compounds. Using this method, it has been verified that the electron density on the nitrogen of anilines determines the ability of these compounds as inhibitor of corrosion for steel in acids [105].

1.14.7. ULTRASONIC TECHNIQUE

The ultrasonic technique [106] is successfully used for the assessment of the corrosion damage. This is specially important for plants where the testing needs to be done without unnecessary shut down for inspection or testing. Generally, two methods of ultrasonic inspection are employed :- reflection and resonance. By the reflection method, the pin points of the position of many different types of internal flaws, e.g. stress corrosion cracking, pits and fatigue cracks etc. are searched. The resonance method measures the flaws which are perpendicular to the direction of ultrasonic beam.

1.14.8 HYDROGEN PERMEATION TECHNIQUE

Atomic hydrogen is produced, when metals are in contact with acids. Before these combine to produce hydrogen molecules, a fraction may diffuse into the metal.

Inside the metal, the hydrogen atoms may combine to form molecular hydrogen. Thus a very high internal pressure builds up. This leads to heavy damage of the metal. This is known as "*Hydrogen embrittlement*".

This phenomenon of hydrogen entry into the metals can occur in industrial processes like pickling plating, phosphating etc. Hydrogen permeation depends on the nature of the acid used and it has been shown [107] that hydrogen permeation decreases in the order $HCl > H_2SO_4 > H_3PO_4 > HClO_4$ for concentration greater than O.5N.

A typical cell for permeation studies was introduced by Devanathan [108] et. al. in which the hydrogen entered, is ionized and recorded as permeation current. The effect of inhibitors on the permeation of hydrogen has assumed remarkable importance in the pickling processes. The inhibitors protect the metal and the entry of hydrogen into the metal is also restricted.

An inhibitor can be considered as completely effective only if it simultaneously inhibits metal dissolution and hydrogen permeation into the metal. Bockris et. al. [109] showed that naphthalene increases the rate of hydrogen penetration into iron. It has also been shown that thiourea and its derivatives act as good inhibitors for iron and steel but stimulate hydrogen penetration [110, 111]. This has been interpreted as due to the formation of hydrogen sulphide. Antropov et. al. [112] studied extensively the effects of numerous inhibitors on the corrosion of iron and on the diffusion of hydrogen through the metal. They showed that pyridine derivatives practically eliminate the diffusion of hydrogen through iron membranes. The behaviour of the inhibitors with regard to hydrogen permeation can be understood by measuring the permeation current with and without inhibitors. Those compounds which when added to the corrosive medium reduce the permeation current are regarded as good inhibitors of the metal concerned.

Other methods of evaluating the hydrogen permeation consist in the determination of brittleness of the metal previously subjected to acid attack in inhibited solution or charged cathodically with hydrogen in acid solutions containing the inhibitors under study [113].The percentage of inhibition of hydrogen penetration

is given by :–

$$I\,E\ (\%) = \frac{N_{inhib} - N_0}{N_{inhi} - N_0} \times 100$$

Where

N_{inhi} = the fracture data determined on metal specimen in absence of adsorbed hydrogen.

N_0 = the fracture data after cathodic charging with hydrogen in the absence of inhibitor

N_{inhib} = the fracture data after cathodic charging in the presence of inhibitor.

1.14.9 ELECTROCHEMICAL NOISE ANALYSIS (ENA)

The noise resistance defined as the ratio of the standard deviation of the potential noise and the current noise has been emperically correlated to the polarization resistance in order to calculate the corrosion rate [114]. The corrosion of pure iron was studied by electrochemical potential noise measurements in 1N H_2SO_4 containing dibenzylsulphoxide and phenyl thiourea [115].

1.14.10 QUARTZ CRYSTAL MICROBALANCE (QCM) METHOD

This method is superior in the sense that it is used to monitor mass change (sensitivity = ng $cm^{-2)}$ as well as electrochemical change during corrosion process. Pickering et. al. [116] have studied the performance of Benzotriazole, other triazoles and triazole - iodide on the corrosion of copper and copper alloy in sulphuric acid solution by applying QCM and Scanning Tunnelling Microscopy (STM).

1.15 INHIBITORS FOR STEEL CORROSION IN ACID MEDIA

Inhibitors play an important role in controlling the corrosion of steel [117, 118]. From 19th century onwards the vegetable wastes, plants extracts [119, 120] were used as inhibitors. Several reviews on organic inhibitors [121 - 123] and organic sulphur compounds [124] have been published. Several books have been published

on this subject [125, 126]. Besides, this university of ferrara, Italy conducts a Symposium on corrosion inhibition once in five years [127]. All the International Seminars on corrosion discuss the development and application of corrosion inhibitors [128 - 129]. Various books on corrosion review the subject in a precise manner [130 - 131]. The European Federation of corrosion, working party on corrosion inhibitors developed a report on corrosion inhibitors describing mechanism, test methods, current research and application in various industrial fields [132].

The recent development on inhibitors study has been described in a review article [133]. The major use of inhibitors in acid solutions is in pickling processes [134, 135], for removal of rust, scale and corrosion products. The main requirement of the inhibitors is that it should neither decompose during the life of the pickle nor increase hydrogen adsorption [136] by the metal. It should not lead to the formation of surface films with electrically insulating properties that might interfere with subsequent electroplating or other surface treatments. Pickling inhibitors require a favourable polar groups by which the molecules can attach itself to the metal surface. These include N, S and O containing organic compounds groups. The size, orientation and shape of the molecule play a part in the effectiveness of inhibition [137]. The surface charge on the metal and its constituents effect the relative strength of the adsorbed bond and corrosion inhibition. Granese and Rosales [138] elucidated the mechanism of corrosion inhibition of iron and steel in HCl media by nitrogen containing organic compounds like acridine hexamethylene, quaternary ammonium sulphate etc. at 85°C.

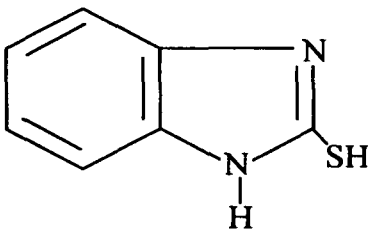
The anion of the pickling acid may also take part in the adsorbed film accounting for differing efficiencies of inhibition for the same compound in HCl as compared to H_2SO_4 [139]. Pickling inhibitors may act as a good inhibitor for iron but not for other metals or vice versa due to specific electronic interactions of polar groups with the metal. Temperature also plays a significant role in affecting the inhibition efficiency [140, 141] e.g., O - tolylthiourea in 5% H_2SO_4 acts as a good inhibitor at elevated temperatures than at room temperature due to increased adsorption.

In USSR acid inhibitors are made by the use of industrial by-products. Katapan,

inhibitor which is alkylbenzyl pyridine chloride [142] and its analogues are efficient in preventing the corrosion of high carbon steels.

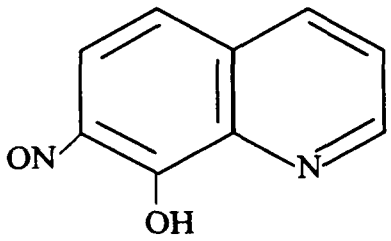
Compounds containing N or S have shown vast applications as corrosion inhibitors [143]. Machu [144] has shown the use of S - containing compounds for H_2SO_4 and N containing compounds for HCl solutions. Hackerman [145] gave the idea that higher percentage of orbitals of the free electrons on the N atom leads to inhibitive action. N - containing compounds used as acid inhibitors include heterocyclic bases such as pyridine, quinoline and various amines [146, 147], S - containing compounds like thiourea and its derivatives, mercaptans and sulphides in concentrations 0.003 - 0.01% give 90% protection [148, 149]. According to Every and Riggs [150], a mixture of N and S containing compounds are better than either type alone. Highly substituted N atoms may increase the inhibition efficiency due to increase of electron density. Alkyl substitution of N atom or p - position of aromatic nucleus improve inhibition efficiency in contrast to meta derivatives. The influence of anions such as I^- and SH^-, in the promotion of pronounced inhibiting action by organic cations in acid solutions is well known [151, 152].

The inhibiting action of pyrrole and its derivatives was investigated in 5N HCl and 5N H_2SO_4 at 20° C by weight loss and polarization methods. The inhibition efficiency was found to be dependent on the dipole moment and pK value [153]. Balezin et. al. [154] studied the inhibitive action of 2 - mercapto-benzimidazole (1) on mild steel. They found it to be effective for mild steel in 1N H_2SO_4 up to 70° C.



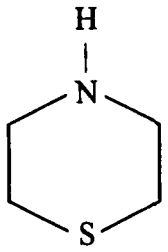
(1)

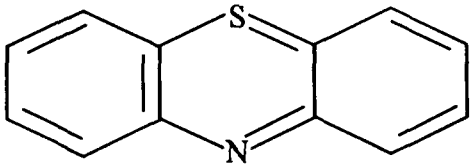
Lee [155] evaluated the corrosion inhibiting effect of 7 - nitroso - 8 - hydroxyquinoline (2) against mild steel in hydrochloric acid solution. It exhibited greater than 90 % efficiency.

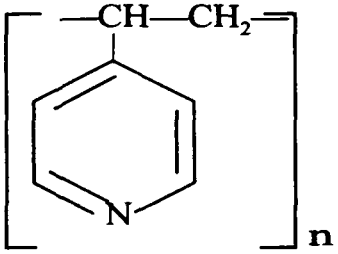


(2)

The use of thiomorpholine (3), phenothiazine derivatives (4) and vinylpyridine polymers (5) as potential pickling inhibitors for ferrous metals has been reported in *US patents [156 - 158]*.

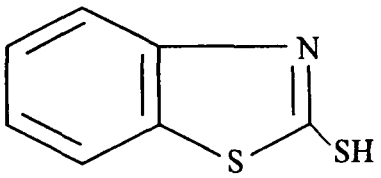






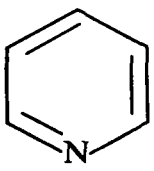
(3) (4) (5)

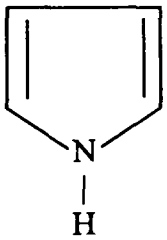
Singh and his co-workers [159] reported about 97 % efficiency of 2 - mercapto-benzothiazole (6) at the concentration of 6 x 4 x 10^{-4} M in 1N H_2SO_4 at 40° C.

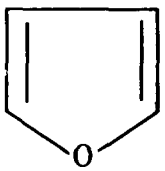


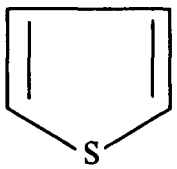
(6)

The inhibitive action of pyridine (7), pyrrole (8), furan (9) and thiophene (10) was investigated by galvanostatic measurement for Fe -1 N H_2SO_4 system. Thiophene exhibited maximum efficiency among the heterocyclics examined [160].





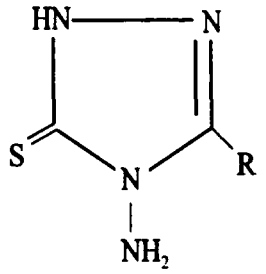




(7) (8) (9) (10)

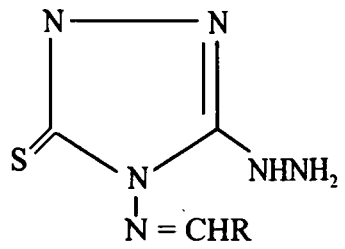
The corrosion of mild steel in 2.5 N H_2SO_4 containing 1 X 10^{-2} M concentration

of 3 - substituted - 4 - amino - 5-mercapto 1, 2, 4 - triazolines (11) was studied [161]..



(11)

The inhibition efficiency of these triazolines was found to increase on introducing electron donar substituents at position - 3. p - methoxyphenyl substituted triazoline showed maximum efficiency among the inhibitors studied, 4 - amino - 3 - hydrazino - 5 - thio - 1, 2, 4 - triazole and some of its derivatives (12) were studied as corrosion inhibitors by Abdel - nabey et. al. [162]. They also found that efficiency of these inhibitors increases on increasing the electron density at active centres of the inhibitors.



(12)

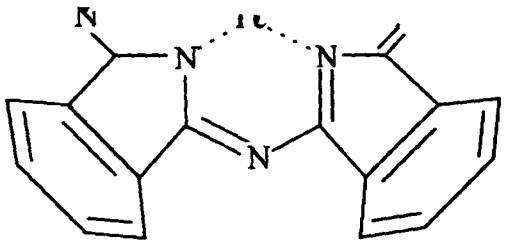
(a) R = H (d) R = C_3H_7

(b) R = CH_3 (e) R = C_6H_5

(c) R = C_2H_5 (f) R = $C_6H_4OCH_3$

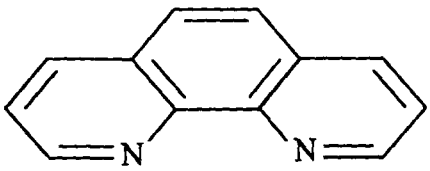
(g) R = C_6H_4Cl

The effectiveness of some macrocyclic compounds [163]such as porphyrins and pthalocyanines as acid corrosion inhibitors for steel was investigated by potentiostatic and AC impedance methods. Pthalocyanines (13) gave 82 % efficiency at 25°C in acid chloride environment (pH = 2).



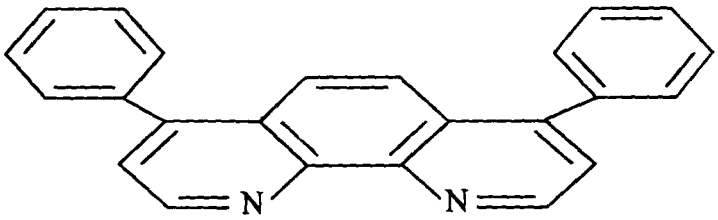
(13)

1,10 - phenanthroline (14) was examined as corrosion inhibitor for mild steel by gasometric and gravimetric methods [164]. The maximum efficiency was found to be 92.1 % and 92.5 % in 1N H_2SO_4 and 1N HCl respectively at 3 X 10^{-3} M concentration.



(14)

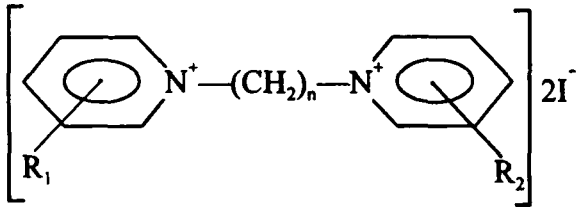
Anderson et al [165] examined the effectiveness of 4, 7 - diphenyl - 1,10 - phenanthroline (15) in acid medium. They found that the inhibiting action of this compound is attributed to the presence of π - electrons of the aromatic rings.



(15)

The inhibition efficiencies of 1,1' - alkylene bispyridinium compounds (16) have been studied for the corrosion of mild steel in 1N H_2SO_4 The inhibitors namely 1,1'- ethylene - 3, 3' - dimethyl bis - pyridiniumiodide and 1, 1' - ethylene - bispyridiniumiodide showed 87.8 % and 86.7 % efficiencies in concentration ranges

of 250 and 1500 ppm respectively at 30° C.



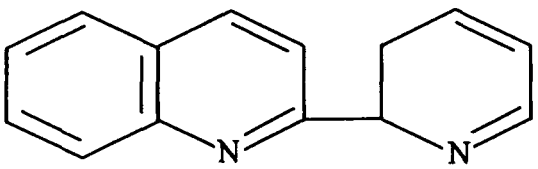
(16)

R_1 = R_2 = H, CH_3, COOH etc.

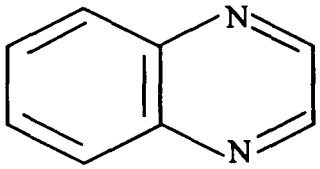
n = 1, 2, 3 etc.

The authors have found that substitution in the pyridine ring has a pronounced effect on the inhibition efficiency [166].

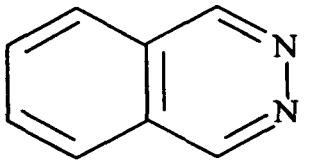
The influence of some heterocyclic compounds containing more than one nitrogen atoms in their molecules on corrosion of carbon steel in 1N HCl was investigated by Trabanelli and co - workers [167] with a view to establish correlation between molecular structure and the inhibition efficiency of the various compounds. Among the examined substances 2, 2 '- Biquinoline (17), Quinoxaline (18), Quinozoline (19) and 2 - mercaptopyrimidine (20) showed good inhibiting efficiencies (80 - 90 %) at 25 - 60°C temperature.



(17)



(18)



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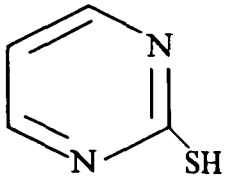
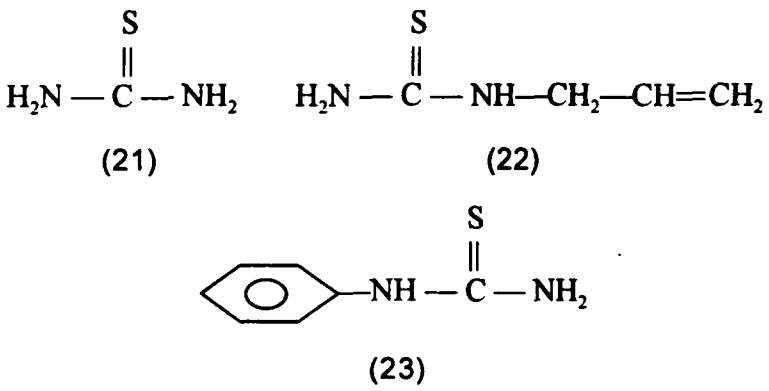


(20)

The inhibitive action of thiourea (21), allylthiourea (22) and n-phenyl thiourea (23) on the corrosion behaviour of martensitic 410 stainless steel in 1N H_2SO_4 was investigated by weight loss and potentiodynamic polarization methods. n-phenylthiourea reduced the corrosion rate most but thiourea reduced the least corrosion rate [168].



(21) (22)

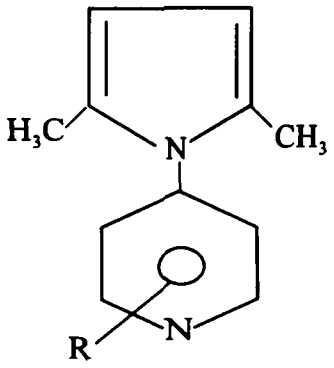
(23)

Sethumadhavan and his co-workers [169] studied 1, 10 - phenanthroline as corrosion inhibitor for mild steel in pure sulphuric acid and found 87 % efficiency at room temperature in 1 x 10^{-2} M concentration.

Sankarapapavinasam [170] studied cis and trans 2, 6 - diphenyl - 4 - tetra - hydrothiopyrones as corrosion inhibitors for mild steel in sulphuric acid.

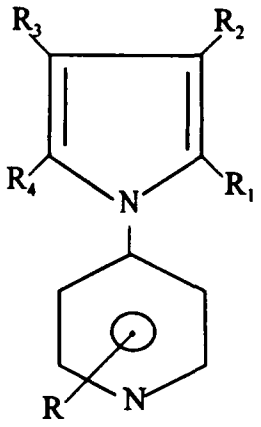
Granese et. al. [171] studied the inhibition action of some nitrogen containing heterocyclic compounds such as pyridine, quinoline, acridine and their n-hexadecyl derivatives in HCl media by electrochemical and surface analysis. They reported that the efficiency of these compounds increases with number of aromatic systems and electrons availability in the molecules.

Stupnisek et. al. [172] investigated the inhibiting action of various substituted N - arylpyrroles (24, 25) on corrosion of iron in strong acid solutions (5 mol. dm^{-3} HCl) using electrochemical methods, with a view of studying the relationship existing between the molecular structure and inhibition efficiencies of pyrroles are significantly influenced by the type and the position of the functional groups. Thus N - arylpyrrole bearing fluorine at ortho position gave better performance than other pyrrole derivatives.



(24)

R = halogen at ortho para or meta position

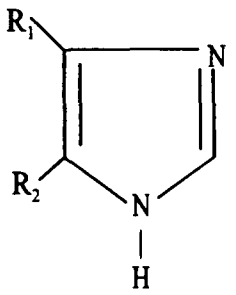


(25)

R = alkyl or halogen

Ihara et al. [173] have analysed the nature and composition of the persistent corrosion protective film formed on iron in acid solutions i.e. 1N $HClO_4$, 1N HCl and 1N H_2SO_4 with triethyl bismuthine by polarization and impedance measurement studies. The protective film comprised monolayer of the inhibitor and anion adsorbed at the solution interface and a film with an outer layer composed of ferrous oxide containing small amount of Bismuth oxide and Chloride ion and an inner layer of metallic Bismuth. The high persistence of the protective film arises from this inner layer.

Raicheva and co - workers [174] investigated several diazoles (26, 27) such as imidazole, benzimidazole and their derivatives as acid corrosion inhibitors of iron and steel. They have found a very good relationship between the structure of diazoles and inhibition efficiency.

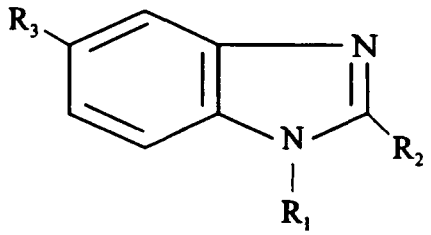


(26)

(a) $R_1 = R_2 = H$

(b) $R_1 = H, R_2 = CH_3$

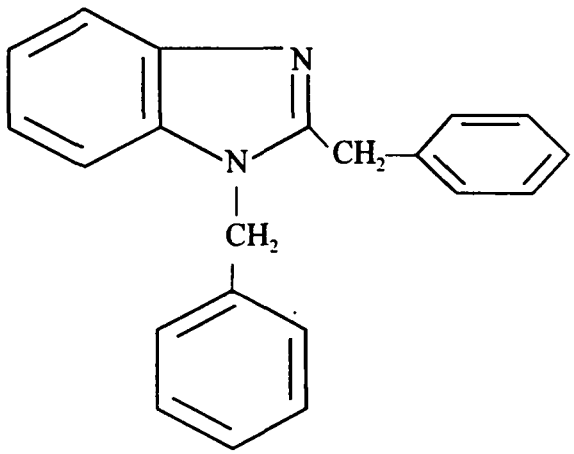
(c) $R_1 = CH_3, R_2 = CH_2OH$



(27)

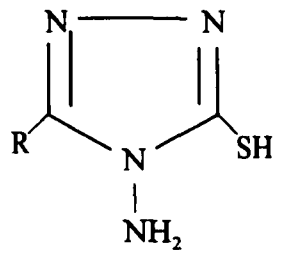
(a)	$R_1 = R_2 = R_3 = H$	(g)	$R_2 = R_3 = R_1 = CH_2C_6H_5$
(b)	$R_1 = R_3 = H, R_2 = CH_3$	(h)	$R_3 = H, R_1 = R_2 = CH_2C_6H_5$
(c)	$R_1 = R_3 = H, R_2 = NH_2$	(i)	$R_1 = R_3 = H, R_2 = C_6H_5N$
(d)	$R_1 = R_3 = H, R_2 = CH_2OH$	(J)	$R_1 = R_3 = H, R_2 = C_6H_4NH_2$
(e)	$R_1 = R_3 = H, R_2 = C_6H_5$	(k)	$R_1 = R_3 = H, R_2 = NO_2$
(f)	$R_1 = R_3 = H, R_2 = CH_2C_6H_5$	(l)	$R_1 = R_2 = H, R_3 = COOH$

They have concluded that the annelation of the benzene nucleus to the diazole ring increases the protective action of the diazole significantly, thus the inhibition efficiency of benzimidazole (I E 29 %) increased to 96 % in 1, 2 dibenzylimidazole (28).



(28)

The inhibitive action of 4 - amino - 5 - mercapto - 3 - methyl - 1, 2, 4 - triazole (29) on corrosion of mild steel in 1N H_2SO_4 and 1N HCl was investigated by potentiodynamic polarization, AC impedance and hydrogen permeation methods [175]. The results of the investigations indicated the improved performance of this compound in H_2SO_4. The inhibitor was also found to be very effective in bringing down the hydrogen permeation current considerably in both the acid solutions.



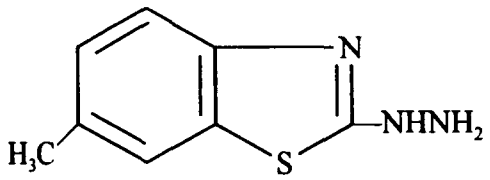
(29)

R = CH_3

Corrosion inhibition of carbon and low alloy steel in sulphuric acid solution was studied by 2 - mercapto - pyrimidine derivatives [176]. Arab and co-workers have studied the performance of S - alkylisothiouronium iodides on the inhibition of the acid corrosion of steel in acid media [177].

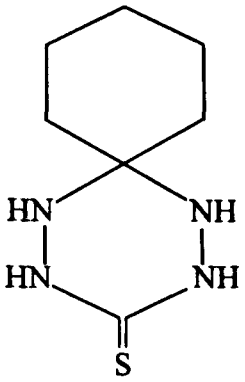
The use of fatty acid ethoxylate as the corrosion inhibitors was well studied on the C-steel in sulphuric acid solutions [178]. Cizek [179] reviewed the use of inhibitors in acidizing process.

Ajmal et. al. [180] studied the inhibitive action of 2 - hydrazino - 6 - methyl - benzothiazole (30) on the corrosion of mild steel in acidic solutions. They found that this compound acts as a mixed inhibitor in 1N H_2SO_4 and behaves predominantly as cathodic inhibitor in 1N HCl. They have also found that inhibitor effectively inhibits permeation of hydrogen through mild steel.



(30)

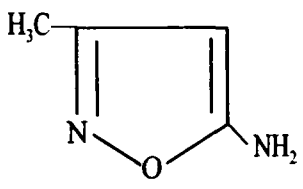
Quraishi et al. [181] has studied the influence of 1, 2, 4, 5 - tetraazospiro (5,5) -undecane - 3 - thione (31) on the corrosion of mild steel in 1N HCl and 1N H_2SO_4 by weight loss, potentiostatic polarization, hydrogen permeation and electrocapillary methods. This compound has given better performance (90 % IE) in HCl than in H_2SO_4 (84.6 % IE) at 500 ppm concentration and it was found to act as a mixed inhibitor.



(31)

Formation of composite film on iron by Bismuth (III) chloride and benzyl thiocyanate in sulphuric acid was studied by Ohi and co-workers [182]. The inhibition efficiency of n - decylamine on the corrosion of low carbon steel in 1N sulphuric acid at different temperature 25 - 55° C has been investigated potentiokinetically. The compound showed 95 % IE at 25° C, and 67.5 % of inhibition efficiency at 55°C at 1 X 10^{-1} ml *concentration* [183].

The inhibition efficiency of some heterocyclic organic compounds viz. 3 - methyl 5 - aminoizoxazole (32), 3, 4, dimethyl - 5 - aminoizoxazole (33), 4 - methyl - 5 - oxazolecarboxamide (34), 2 - acetylamino - 5 - sulphamoyal - 1, 3, 4-thiadiazole (35), 2 - acetylamino - 5 - mercapto - 1, 3, 4 - thiadiazole (36), 4 - methyl - 5 - imidazole carbaldehyde (37) was investigated on iron in hydrochloric acid at 20° C and in sulphuric acid at 20 - 60° C [184]. Among these 4 - methyl - 5 - imidazole carbaldehyde showed best inhibiting effect on iron in 5N HCl solutions.



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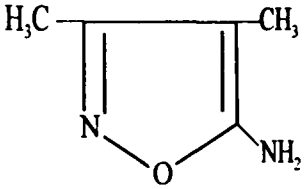
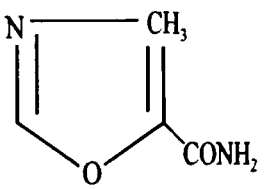


(33)



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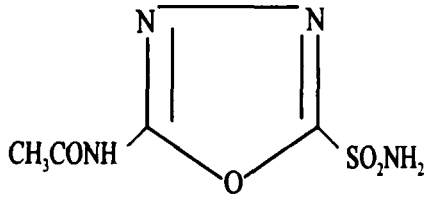

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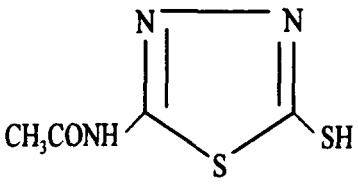

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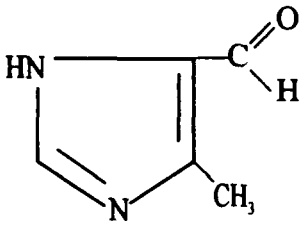
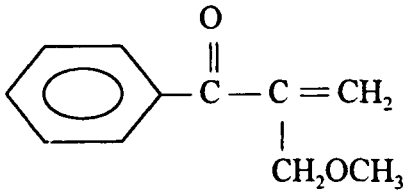


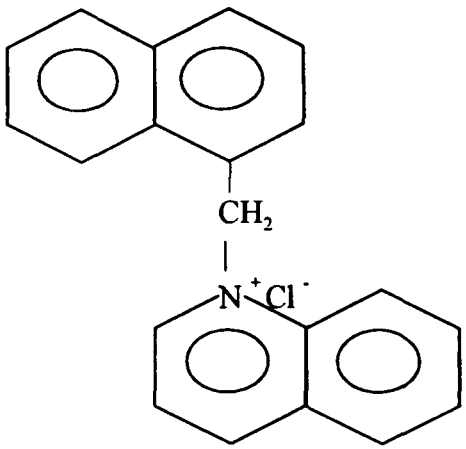
(37)

The efficiency of alkyltriazoles compounds as inhibitors of armco iron corrosion and hydrogen embrittlement has been studied in 1N HCl solution [185] by weight loss, polarization and impedance measurement. The Dodecyl - 1, 2, 4 - triazole has shown best results giving an IE of 90%.

The efficiency of 2- benzoyl- 3 -methoxy - 1 - propane (38) and Napthylmethyl quinolinium chloride (39) was evaluated for oil - field tubular steel corroding in HCl at 60°C and 125°C [186].

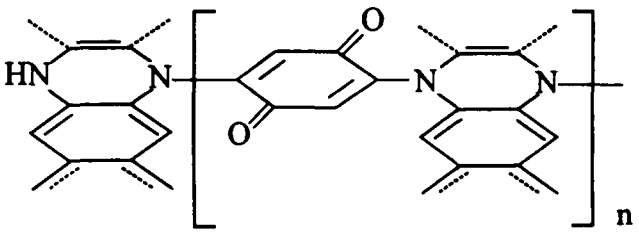


(38)



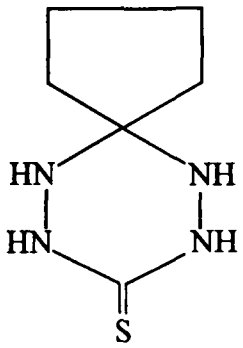
(39)

The corrosion inhibition performance of a polymer Polyamino - benzoquinone (40) was studied in 1N HCl and H_2SO_4 by UV, EIS, Polarization and hydrogen permeation studies. Weight loss studies for 2 hour duration at room temperature. The polymer exhibited 94.7 % IE in H_2SO_4 whereas 83.4 % in HCl at 500 ppm. Polarization studies show that it is a mixed inhibitor. The compound also brought about significant reduction in hydrogen permeation current in H_2SO_4 [187].

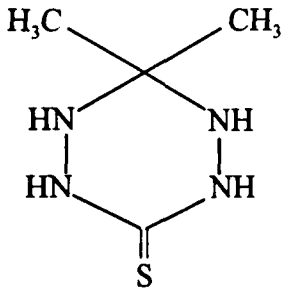


(40)

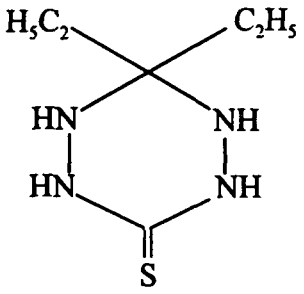
The influence of Cyclopentyl-tetrahydro-aza-thione (41), Dimethyl-tetrahydro-aza-thione (42) and Ethyl-methyl-tetra hydro-aza-thione (43) on mild steel corrosion in HCl and H_2SO_4 was studied, all compounds have shown better inhibition in HCl and showed mixed type of inhibiting action [188].



(41)

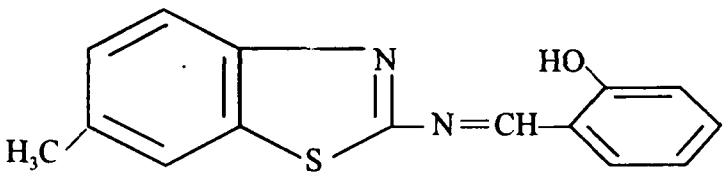


(42)



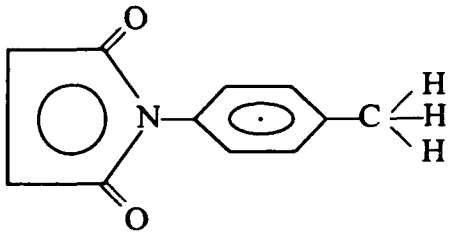
(43)

Inhibition properties of 2- salicylidene - amino - 6 - methyl - benzothiazole (44) towards the mild steel corrosion and hydrogen permeation in acidic solutions was investigated by Quraishi et. al. [189]. The compound showed 97.7 % inhibition efficiency in HCl and 83.4 % in H_2SO_4 solutions. The compound was also found to inhibit the diffusion of hydrogen into the metal.

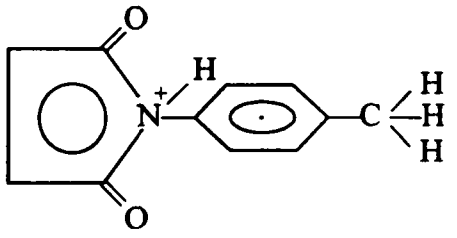


(44)

The adsorption behaviour of N - p -tolyl phenylmaleimide (45, 46) on inhibition of iron corrosion was studied by an impedance technique in 0.1M H_2SO_4 and 0.005M Na_2SO_4. The compounds were found to obey Frumkin type adsorption isotherm [190].



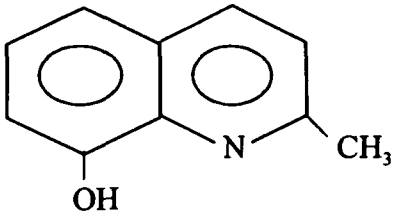
(45)



(Protonated form in acid)

(46)

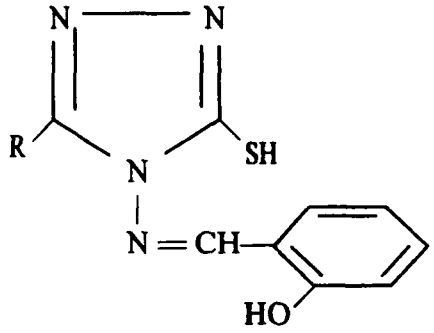
The inhibition and adsorption behaviour of 8 - hydroxyquinaldine (47) on iron in 1N sulphuric acid solutions was studied at 20°C. It exhibited 99 % I E at a bulk inhibitor concentration of 0.1 - 10 m mol / l [191].



(47)

The influence of some quaternary salts such as Benzotri-phenyl phosphonium chloride $(BTPhP)^+Cl^-$, Tetrabutyl ammonium bromide $(TBuA)^+Br^-$ and cetyltri-methylammonium bromide $(CTMA)^+Br^-$ towards the corrosion of mild steel in 3M H_2SO_4 solution was studied by using EIS and classical linear polarization techniques by Morad et. al. [192]. The mechanism of inhibition was explained in the light of electrostatic adsorption involving the changes in the structure of the electrical double layer (TBuABr), formation of a multimolecular barrier on the steel surface (CTMA Br) and interaction of the π system with the steel surface (BT Ph PCl).

Muralidharan et.al. [193] have further synthesized a few anils (48) by condensing 3 - alkyl - 4 - amino - 5 - mercapto - 1, 2, 4 - triazoles with salicyldehyde with a view to investigate the inhibitive action of these compounds on the corrosion of mild steel in acidic medium. They have found that all these compounds show better performance than the corresponding amines.



(48)

R_1 = H, 2. R = CH_3, R = C_3H_7

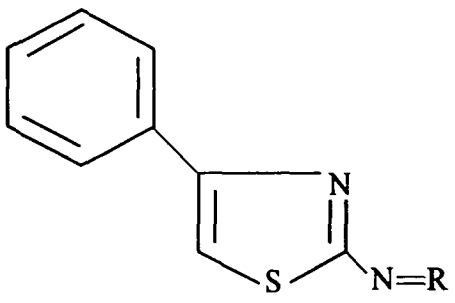
Tetrabutyl ammonium iodide, cetyl pyridinium bromide and cetyl trimethyl ammonium bromide were studied as corrosion inhibitors for mild steel in H_2SO_4 [194]. The inhibition efficiency of these compounds increased with the increase in temperature.Their inhibition efficiencies varied with different inhibitors in the following order.

Tetrabutyl ammonium iodide > cetyl pyridinium bromide > cetyl trimethyl ammonium bromide

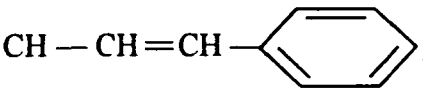
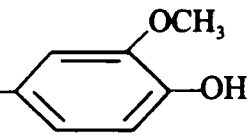
The effectiveness of 2 - amino - 4 - phenyl thiazole and its three anils (49) were evaluated for the corrosion of mild steel in HCl by weight loss potentiodynamic polarization and auger electron spectroscopic methods. Their inhibition efficiencies followed the order :-

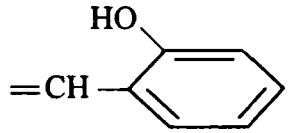
2 - cinnamalidene amino - 4 - phenylthiazole > 2 - vanillidene amino - 4 - phenylthiazole > 2 - salicylidene amino - 4 - phenythiazole > 2 - amino - 4 - phenyl thiazole.

The cinnamalidene derivative exhibited 98 % I E at 60°C at concentration of 300 ppm [195].

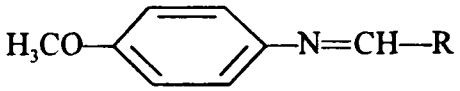


(49)

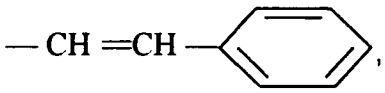
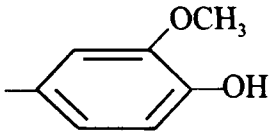
1. R = H_2, 2. R =  , 3.R = 

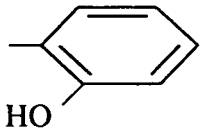
4. R = 

Aromatic schiffs bases such as cinnamaldehyde -p-anisidine vanillin - p - anisidine and Salicyldehyde - p - anisidine (50) were investigated as acid corrosion inhibitors in 1N HCl and H_2SO_4 for mild steel by Quraishi et al [196]. Among them cinnamaldehyde - p - anisidine gave 93.8 % inhibition efficiency in 1N HCl at a concentration as low as 300 ppm. All schiffs bases gave better performance in 1N HCl than in 1N H_2SO_4.



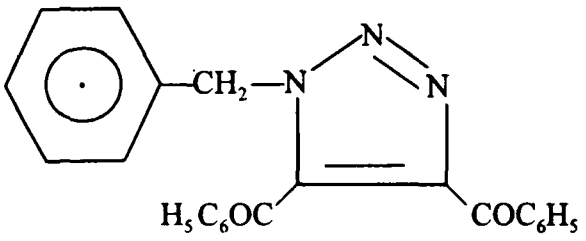
(50)

1. R =  , 2. R = 

3. R = 

Some indole derivatives [197], Dithizone and Thiosemicarbazides [198] 5 - amino and 5 - chloro - indole [199] Benzotriazole [200] and 2 - amino benzene arsonic acid [201] were studied as corrosion inhibitors in H_2SO_4 for steel.

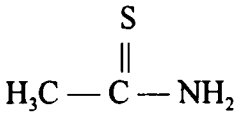
The inhibitive effect of 1 (Benzyl) 1 - H - 4, 5, di benzoyl - 1, 2, 3 - triazole (51) on the corrosion of mild steel in acid medium was investigated by Tafel polarization technique, AC impedance measurement and continuous linear polarization resistance method. The corrosion rate of mild steel in 1% HCl was reduced by more than 95 % in presence of 50 ppm of this compound. This inhibitor showed mixed inhibition effect with a significant shift in the free corrosion potential to cathodic direction [202].



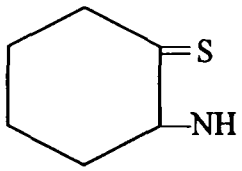
(51)

The synergistic effect of 2 - mercapto benzimidazole and some cations was studied on corrosion of mild steel in acid solution [203]

Linear (52)and cyclic (53)Thiocarbamide such as - Thiocarbamide, Thiobenzamide, N - ethyl thiocarbamide, tetra methyl thiocarbamide, 2 - imidazolidine thione, N - methylthiocarbamide, 4, 5 dihydroxy - 2 - imidazolidinethione and thioacetamide were evaluated as effective corrosion inhibitors in 1 M HCl. The inhibiting effect of these compounds was found to increase with the increase in the temperature. All of these compounds are found to adsorb on metal surface through S - atoms [204].

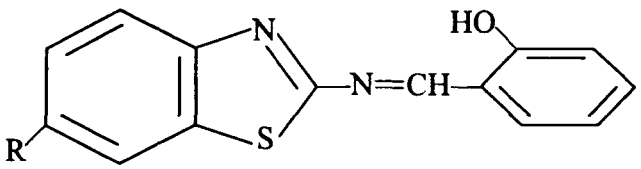


(52)



(53)

The heterocyclic anils 2- salicylidene-aminobenzothiazole and its derivatives (54) were investigated to evaluate their efficiency as corrosion inhibitors for mild steel in HCl at 100 - 500 ppm concentration at 35 - 60°C temperature. Among them chloro derivatives exhibited highest IE of 98 %. The analysis of inhibited mild steel coupons by auger electron spectroscopy revealed that these compounds are adsorbed on mild steel surface through hetero atoms like N, S or Cl and inhibit corrosion [205].

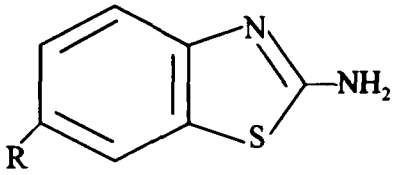


(54)

1. R = H, 2. R = CH_3, 3. R = Cl

Influence of 2- amino benzothiazole and its substituted derivatives (55) was

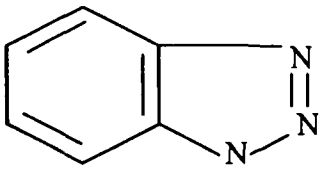
studied on mild steel corrosion in H_2SO_4 at 35- 60°C temperature. Among these chloro derivatives showed best performance at 500 ppm concentration by reducing the hydrogen permeation current as well as inhibiting the corrosion of mild steel (97 % IE) [206].



(55)

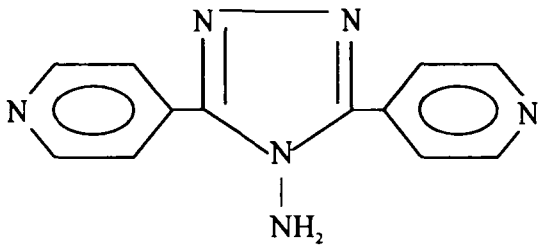
1. R = H, 2. R = CH_3, 3. R = OCH_3, 4. R = Cl

The inhibitive performance of Benzotriazole (56) on the corrosion of stainless steel (18 cr - 9 Ni - Ti) was studied in acidic chloride solution using potentiodynamic polarisation, electrochemical impedance spectroscopy and scanning electron microscopy. The inhibitive action of this compound was observed due to the blocking of anodic and cathodic areas [207].



(56)

The corrosion inhibitive behaviour of 3, 5 - bis (n - pyridyl) - 4 - amino - 1, 2, 4 - triazoles on mild steel in 1M HCl medium was studied by Mernari et. al. [208].



(57)

1.16 AIMS AND OBJECTIVES

In the present investigation 22 new organic corrosion inhibitors belonging to four different classes of organic compounds have been synthesized with following aims and objectives: –

* To study the inhibitive action of the synthesized organic compounds on corrosion of mild steel in acidic environments.
* To investigate the mechanism of corrosion inhibition using potentiodynamic polarization and ac impedance technique.
* To investigate the effectiveness of synthesized inhibitors for permeation of hydrogen through mild steel in acid solution.
* To study the influence of molecular structure on corrosion inhibition.
* To analyse the nature and composition of the adsorbed film of inhibitor through auger electron spectroscopy and Scanning electron microscopy.

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CHAPTER 2

EXPERIMENTAL

2.0 MATERIAL

2.1 TEST SPECIMEN

The mild steel sheets used for the investigation had the following composition :–

C	Mn	Si	S	P	Fe
0.14	0.35	0.17	0.025	0.03	Rest

2.2 TEST SOLUTION

A. R. grade sulphuric and hydrochloric acids and double distilled water was used to prepare all the solutions required for the experiments. 1-2 % ethanol or acetone was used to dissolve the inhibitors.

2.3 INHIBITORS USED

1. 2, 3, 9, 10 - tetraphenyl - 6, 13 - dithia - 1, 4, 5, 7, 8, 11, 12, 14 - octaaza-cyclotetradecane - 2, 4, 7, 8, 10, 12 - hexaene **(PTAT)**
2. 3, 4, 9, 10 - tetraphenyl - 7, 12 - dithia - 1, 2, 5, 6, 8, 11 - hexaaza - cyclobidecane-2, 4, 7, 8, 10, 12 hexaene **(PTAB)**
3. 3, 4, 9, 10 - tetraphenyl - 7, 12 - dioxa - 1, 2, 5, 6, 8, 11 - hexaaza-cyclobidecane - 2, 4, 7, 8, 10, 12 hexaene **(POAB)**
4. 7, 14 - dimethyl - 5, 12 - dioxo - 1, 4, 8, 11 - tetraaza - cyclotetradeca - 1, 7 - diene **(MOAT)**
5. 2, 3 : 9, 10 - dibenzo - 7, 14 - dimethyl - 5, 12 - dioxo - 1, 4, 8, 11 - tetraaza - cyclotetradeca - 1, 7 - diene **(BMOAT)**
6. 2, 5, 10, 13 - tetraoxo - 1, 6, 9, 14 - tetraaza - cyclohexadecane **(OAH)**
7. 7, 8 : 15, 16 - dibenzo - 2, 5, 10, 13 - tetraoxo - 1, 6, 9, 14 -tetraaza-

cyclohexadecane **(BOAH)**

8. 3, 4 : 11, 12 - dibenzo - 2, 5, 10, 13 - tetraoxo - 1, 6, 9, 14 - tetraaza-cyclohexadecane **(DBOAD)**

9. 3, 4 : 7, 8 : 11, 12 : 15, 16 - tetrabenzo - 2, 5, 10, 13 - tetraoxo - 1, 6, 9, 14 - tetraazacyclo - hexadecane **(TBOAD)**

10. Phenyl thiobisformamidine **(PTBF)**

11. Tolyl thiobisformamidine **(TTBF)**

12. Anisidyl thiobisformamidine **(ATBF)**

13. 4 - chlorophenyl thiobisformamidine **(CPTBF)**

14. 1, 5 - diphenyl - 2, 4 - dithiobiuret **(DPDTB)**

15. 1 - tolyl - 5 -phenyl - 2, 4 - dithiobiuret **(TPDTB)**

16. 1 - anisidyl - 5 - phenyl - 2, 4 - dithiobiuret **(APDTB)**

17. 1 - chlorophenyl - 5 - phenyl - 2, 4 - dithiobiuret **(CPDTB)**

18. 1 - benzylidene - 3 - thiocarbohydrazide **(BTCH)**

19. 1 - salicylidene - 3 - thiocarbohydrazide **(STCH)**

20. 1 - vanillidine - 3-thiocarbohydrazide **(VTCH)**

21. 1 - cinnamylidene - 3 - thiocarbohydrazide **(CTCH)**

22. 1 - furfurylidene - 3 - thiocarbohydrazide **(FTCH)**

2.4 SYNTHESIS OF MACROCYCLIC COMPOUNDS

2.4.1 SYNTHESIS OF PTAT, PTAB AND POAB

2.4.1.(A) PREPARATION OF THIOCARBOHYDRAZIDE [1]

To a vigorously stirred solution of 250 grams of 100% hydrazine hydrate (5 mol) in 150 ml of water, 76 grams (1 mol) of Carbon disulphide was added dropwise.

The reaction mixture was then heated at reflux for 30 minutes, cooled in ice bath for 30 minutes. The precipitated thiocarbohydrazide was filtered off, washed with ethanol and ether, air dried and crystallized from minimum amount of water acidified with a few drops of concentrated HCl : M.P. = 165° C.

2.4.1. (B) SYNTHESIS OF PTAT, PTAB AND POAB (SCHEME 1.1) [2]

A solution of benzil (0.04 mol) in 30 ml ethanol was added dropwise to a refluxing solution of thiocarbohydrazide or thiosemicarbohydrazide or semicarbohydrazide (0.04 mol) in 30 ml of ethanol, followed by the addition of Conc. HCl (1ml). The mixture was refluxed for 4 - 6 hours and the solution was left for overnight. The precipitate thus obtained was filtered off and then recrystallized with ethanol. Their TLC were obtained in benzene + acetone + ethylacetate (6 : 3 : 1) mixture of solvents. The macrocyclic compounds thus prepared are: -

1. 2, 3, 9, 10 - tetraphenyl - 6, 13 - dithia - 1, 4, 5, 7, 8, 11, 12, 14 - octaaza - cyclotetradecane - 2, 4, 7, 8, 10, 12 - hexaene (PTAT) M.P. = 185°C, R_f = 0.51. I R (KBr) Cm^{-1}, 1590 (C = N, stretch), 1080 (C = S, stretch)

2. 3, 4, 9, 10 - tetraphenyl - 7, 12 - dithia - 1, 2, 5, 6, 8, 11 - hexaaza - cyclobidecane - 2, 4, 7, 8, 10, 12 hexaene (PTAB) M.P. = 100°C, R_f = 0.53.

3. 3, 4, 9,10 - tetraphenyl - 7,12 - dioxa - 1, 2, 5, 6, 8, 11 - hexaaza - cyclobidecane - 2, 4, 7, 8, 10, 12 - hexaene (POAB) M. P. = 198°C, R_f =0.63.

2.4.2 SYNTHESIS OF MOAT, BMOAT, OAH, BOAH, TBOAD AND DBOAD (SCHEME 1.2) [3]

To the 1, 2 - diaminoethylene or 1, 2 - diaminophenylene (0.01 mol) in 50 ml methanol, ethylacetoacetate or succinic acid or pthallic acid (0.01 mol) in 50 ml methanol was added dropwise while stirring continuously for 7 hours. The resultant solid product was then filtered, washed with methanol and dried in air. These compounds are crystallized by the mixture of methanol and ethanol. Their R_f value s were obtained in benzene + ethylacetate (7 : 3) mixture. The macrocyclic compounds thus prepared are: -

4. 7, 14 - dimethyl - 5, 12 - dioxo - 1, 4, 8, 11 - tetraaza - cyclotetradeca - 1, 7 - diene (MOAT) M. P. = 114°C, R_f = 0.57.

5. 2, 3 : 9, 10 dibenzo - 7, 14 - dimethyl - 5, 12 - dioxo - 1, 4, 8, 11 - tetraaza - cyclotetradeca -1, 7 - diene (BMOAT), M.P.=176°C, R_f = 0.62. I R (KBr) Cm^{-1}, 1591 (C = N), 3245 (–NH), 1621 (C = O, cyclic).

6. 2, 5, 10, 13 - tetraoxo - 1, 6, 9, 14 - tetraaza-cyclohexadecane (OAH), M.P. = 144°C, R_f = 0.48.

7. 7, 8 : 15, 16 - dibenzo - 2, 5, 10, 13 - tetraoxo - 1, 6, 9, 14 - tetraaza - cyclohexadecane (BOAH), M.P. = 160°C, R_f = 0.56.

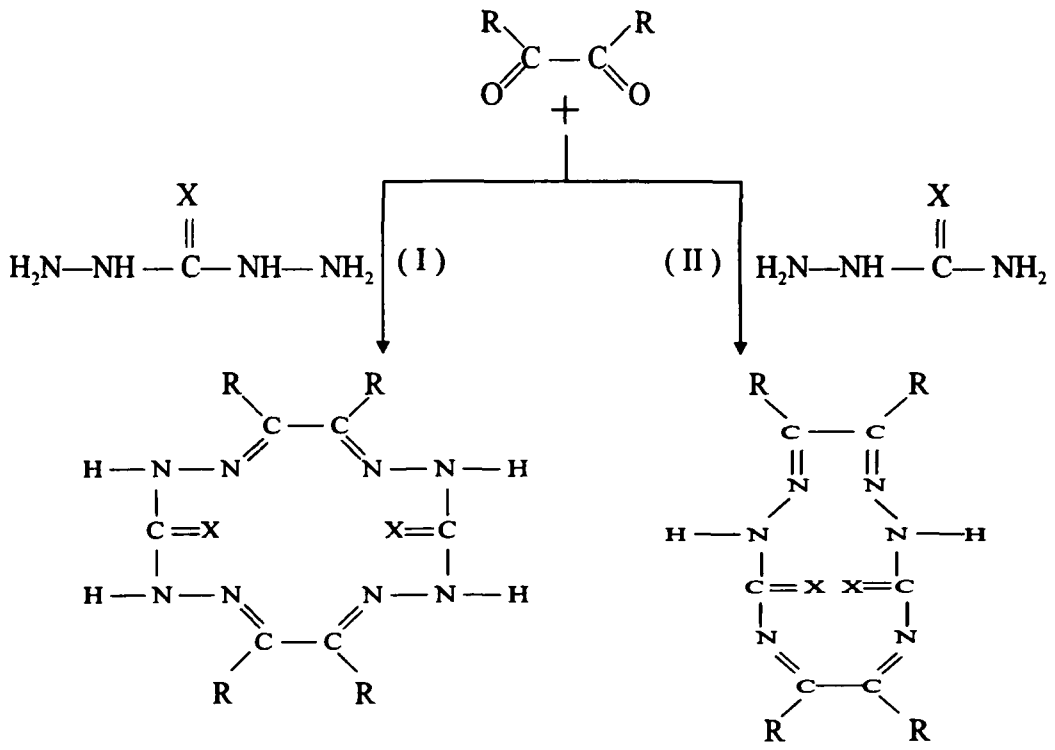
8. 3, 4 : 11, 12 - dibenzo - 2, 5, 10, 13 - tetraoxo - 1, 6, 9, 14 - tetraaza - cyclohexadecane (DBOAD), M.P. = 169°C, R_f = 0.60.

9. 3, 4 : 7, 8 : 11, 12 : 15, 16 - tetrabenzo - 2, 5, 10, 13 - tetraoxo - 1, 6, 9, 14 - tetraazacyclo-hexadecane (TBOAD), M.P. = 203°C, R_f= 0.63.

2.6 SYNTHESIS OF SUBSTITUTED THIOBISFORMAMIDINE (SCHEME - 2)

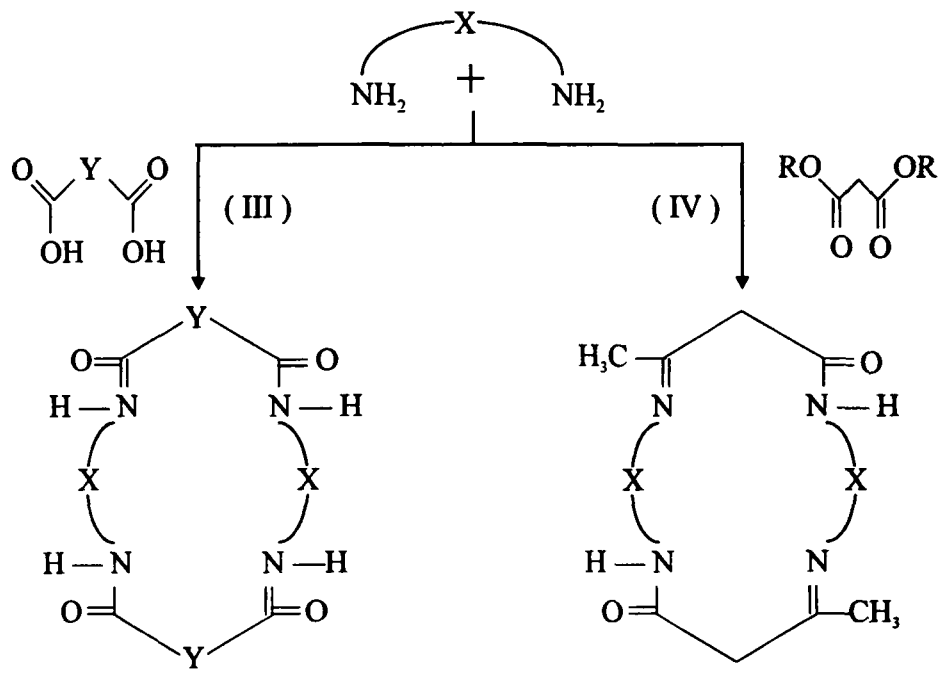
2.5.1 PREPARATION OF P - SUBSTITUTED ARYLTHIOUREA [4, 5]

An appropriate p - substituted aniline (0.1 mol) was dissolved in a mixture of concentrated HCl (9 ml) and water (25 ml) by warming on a water bath. The solution of amine hydrochloride thus obtained was cooled and solid ammonium thiocyanate (0.1 mol) was added.The reaction mixture was then heated for 5 hours on a water bath. Thereafter, the reaction mixture was cooled and the precipitated crude product was filtered, washed with water, dried and crystallized from aqueous ethanol. p - substituted arylthiourea thus prepared are Phenyl thiourea : M.P. = 148°C, p - tolyl thiourea: M.P. = 180°C, p - anisidyl thiourea : M.P. = 209°C, p - chlorophenyl thiourea : M.P. = 174° C.



(I) 1. R = C_6H_5, X = S (PTAT)
(II) 2. R = C_6H_5, X = S (PTAB)
3. R = C_6H_5, X = O (POAB)

SCHEME 1.1



(III) 4. X = $(CH_2)_2$, Y = $(CH_2)_2$ (OAH)
5. X = C_6H_4, Y = $(CH_2)_2$ (BOAH)
6. X = $(CH_2)_2$ Y = C_6H_4 (DBOAD)
7. X = C_6H_4 Y = C_6H_4 (TBOAD)
(IV) 8. X = $(CH_2)_2$ R = C_2H_5 (MOAT)
9. X = C_6H_4 R = C_2H_5 (BMOAT)

SCHEME 1.2

2.5.2 SYNTHESIS OF SUBSTITUTED THIOBISFORMAMIDINES (SCHEME 2) [6, 7]

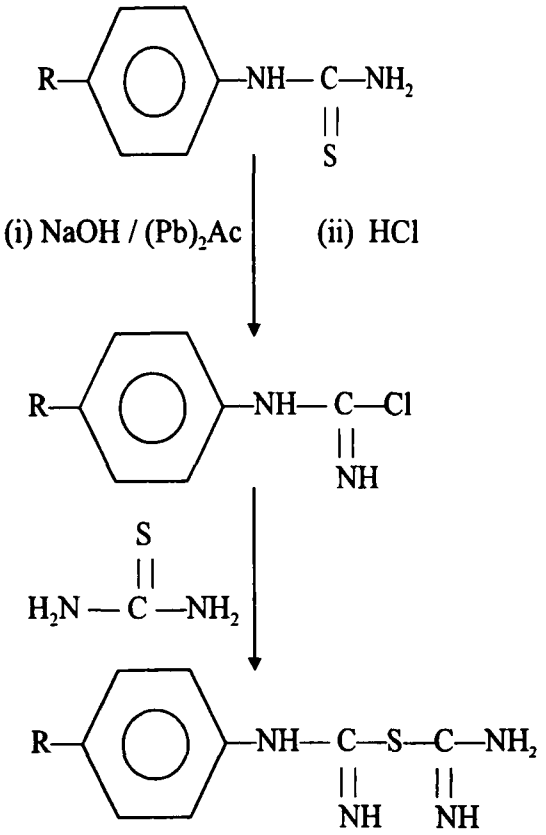
To the alkaline solution of p - substituted arylthiourea (0.65 mol), lead acetate (0.5 mol) was added, this mixture was heated with reflux on water bath for 30 minutes to desulfurize the respective arylthioureas. Black precipitate of sulphur was filtered off and to the filtrate ice cold glacial acetic acid was added dropwise to obtain the precipitate. To this precipitate dry ether was added. To the ethereal layer HCl gas was bubbled to get yellow oily layer. This oily layer was extracted. Thiourea (0.11 mol) and dry acetone was added to this oily layer dropwise to get the precipitate of the substituted thiobisformamidines, after keeping the contents to about half an hour. The precipitate thus obtained was crystallized from the solvent. Their TLC were obtained in the mixture of benzene + ethylacetate (7 : 3). The substituted thiobisformamidine thus prepared are: –

10. Phenyl thiobisformamidine (PTBF) M. P.= 126°C, R_f = 0.44.
    I R (KBr) C m^{-1}, 3245 - 3455 (NH, NH_2), 1590 (C = N, stretch), 1320 (= C – S – C =).
11. Tolyl thiobisformamidine (TTBF), M.P. = 125°C, R_f = 0.51.
12. Anisidyl thiobisformamidine (ATBF), M. P. = 176°C, R_f = 0.40.
13. 4 - chlorophenyl thiobisformamidine (CPTBF), M.P. = 165°C, R_f = 0.64.

2.6 SYNTHESIS OF 1 - SUBSTITUTED DITHIOBIURETS

2.6.1 PREPARATION OF PHENYL ISOTHIOCYANATE [8]

To a round bottomed flask fitted with a mechanical stirrer and surrounded by an ice - salt cooling bath carbon disulphide (0.71 mol) and aqueous ammonia (1.3 mol) were added. Aniline (0.6 mol) was added dropwise while stirring for about 20 minutes. The reaction mixture was allowed to stand for another thirty minutes. To it lead nitrate (0.6 mol) and water (400 c.c.) was added. Thus obtained black mixture was distilled with steam in to a receiver containing 5 - 10 c.c. of 1N sulphuric acid. The distillate (oil) was separated from water and dried over calcium chloride and distilled under reduced pressure B.P. 121°C.



10. R = H (PTBF)
11. R = CH_3 (TTBF)
12. R = OCH_3 (ATBF)
13. R = Cl (CPTBF)

SCHEME 2

2.6.2 SYNTHESIS OF 1 - SUBSTITUTED DITHIOBIURETS (SCHEME - 3) [9,10]

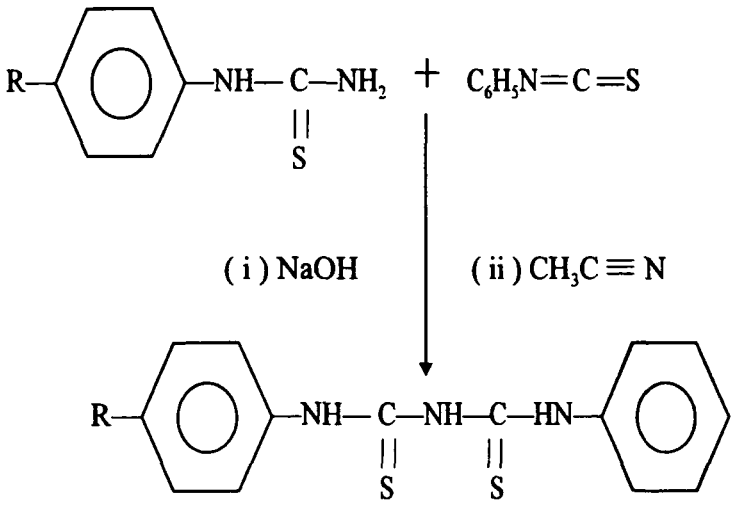
Phenylisothiocyanate (0.025 mol) was added dropwise to the solution of p-substituted arylthiourea (0.025 mol) and powdered sodium hydroxide (0.025 mol) in acetonitrile (15 ml). The reaction mixture was heated to about 60°C and stirred at this temperature for another 30 minutes when a clear solution resulted. The reaction mixture was diluted with water (150 ml) and filtered. The filtrate was acidified with conc. hydrochloric acid (4 ml, 33%) and the precipitated product was collected and redissolved in the minimum quantity of 4% aqueous alkali to remove any unreacted thiourea and filtered. The alkaline filtrate on acidification at 0°C afforded 1 - substituted, 5 - phenyl 2, 4 - dithiobiurets which were recrystallized as needles from ethanol. The TLC were obtained in benzene + acetone + ethylacetate (6 : 3 : 1). Thus prepared substituted dithiobiurets are:-

14. 1, 5 - diphenyl - 2, 4 - dithiobiuret (DPDTB), M.P. = 130°C, R_f = 0.48. IR (KBr) Cm^{-1}, 3320 - 3160 (– NH), 1350 (C – N), 1100 (C = S, stretch)
15. 1 - tolyl - 5 - phenyl - 2, 4 - dithiobiuret (TPDTB), M.P. = 130°C, R_f = 0.56.
16. 1 - anisidyl - 5 - phenyl - 2, 4 - dithiobiuret (APDTB) M.P. = 83°C, R_f = 0.62.
17. 1 - chlorophenyl - 5 -phenyl -2, 4 - dithiobiuret (CPDTB), M.P. = 138°C, R_f = 0.52.

2.7 SYNTHESIS OF SUBSTITUTED THIOCARBOHYDRAZIDES (SCHEME 4)[11]

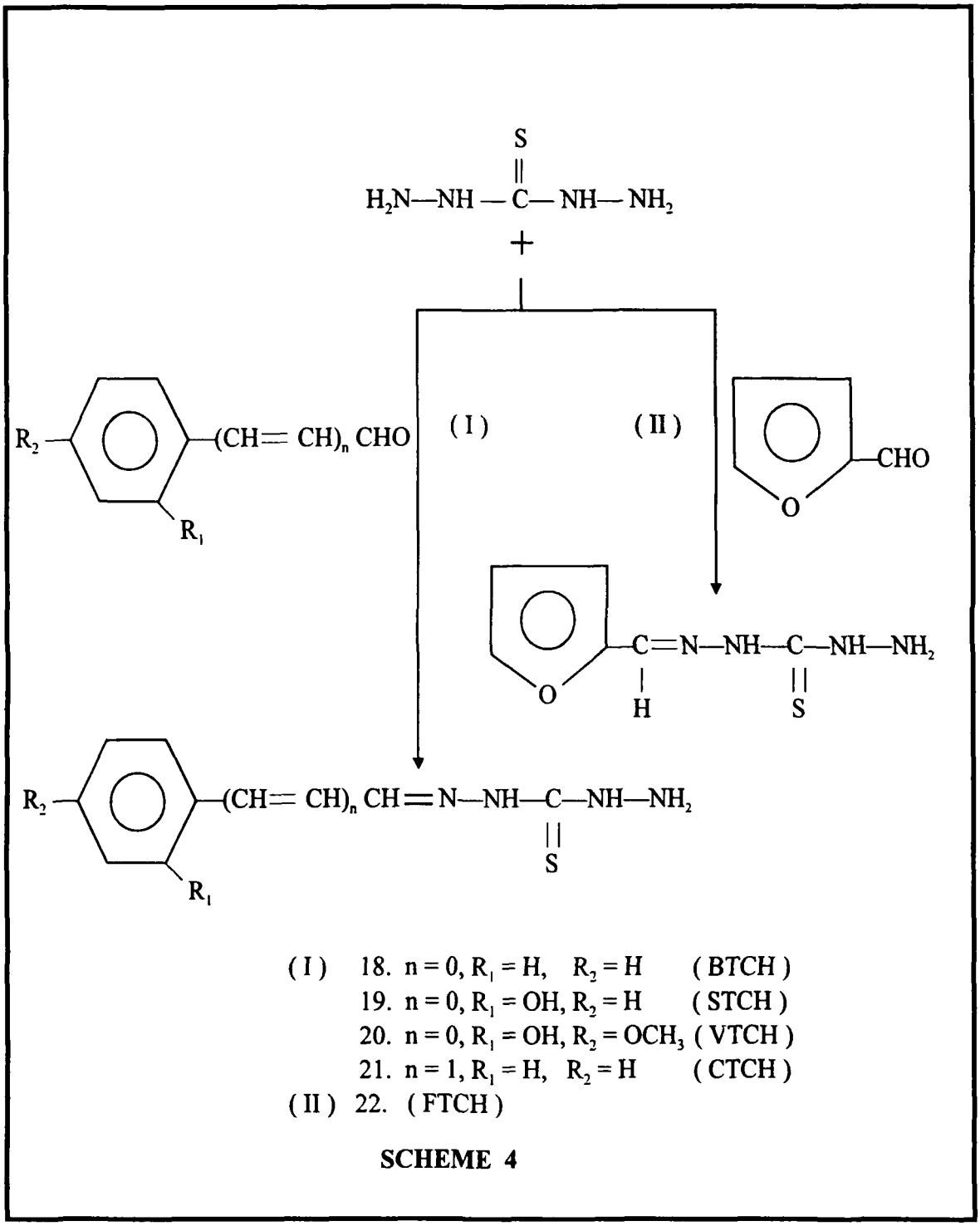
To the warm aqueous solution of thiocarbohydrazide (0.1 mol) alcoholic solution of benzaldehyde, salicyldehyde, vanillin, cinnamaldehyde or furfuraldehyde (0.1 mol) was added dropwise while stirring magnetically for about 30 minutes without further heating. After keeping the mixture overnight precipitate was filtered off and air dried. The compounds were crystallized from alcohol. The compounds thus prepared are:-

18. 1 - benzylidene - 3 - thiocarbohydrazide (BTCH), M.P. = 191°C, R_f = 0.47. IR (KBr) Cm^{-1}, 3245 - 3455 (NH, NH_2) stretch 1100 (C = S) and 1689 (C =N).
19. 1 - salicylidene - 3 - thiocarbohydrazide (STCH), M.P. = 193°C, R_f = 0.53.



14. R = H (DPDTB)
15. R = CH_3 (TPDTB)
16. R = OCH_3 (APDTB)
17. R = Cl (CPDTB)

SCHEME 3



(I) 18. n = 0, R_1 = H, R_2 = H (BTCH)
19. n = 0, R_1 = OH, R_2 = H (STCH)
20. n = 0, R_1 = OH, R_2 = OCH_3 (VTCH)
21. n = 1, R_1 = H, R_2 = H (CTCH)

(II) 22. (FTCH)

SCHEME 4

20. 1 - vanillidine - 3 - thiocarbohydrazide (VTCH), M.P. = 199°C, R_f = 0.62.

21. 1 - cinnamylidine - 3 - thiocarbohydrazide (CTCH), M.P. = 166°C, R_f = 0.48.

22. 1 - furfurylidine - 3 - thiocarbohydrazide (FTCH), M.P. = 185°C, R_f = 0.50.

2.8 TECHNIQUES EMPLOYED

The experimental work was carried out with the help of the following techniques:–

1. Weight loss
2. Potentiodynamic polarization
3. Electrochemical AC impedance
4. Hydrogen permeation
5. Auger electron spectroscopy
6. Scanning electron microscopy

2.8.1 WEIGHT LOSS METHOD

The specimens of the size 2 x 2 x 0.025 cm. were cut from the mild steel sheet and mechanically polished with the 1 / 0, 2 / 0, 3 / 0 and 4 / 0 grades of emery papers. After polishing the specimens were washed with trichloroethylene. The specimens were stored in the dessicator over silica gel. The weight of the specimen was measured before exposing it to corrodent on the single pan Saritorius balance. Weight loss experiments were conducted following the procedures given in the literature [12,13]. During experiments the specimens were fully immersed in 160 ml test solution using beaker of 200 ml capacity. After a definite exposure time the specimens were taken out and washed with distilled water. If there was any corrosion product on mild steel surface it was removed from the surface by mechanical rubbing with a rubber cork. The specimens were then dried and loss in weight was recorded. The thermostatic water bath was used for carrying out the weight loss experiments at higher temperatures. Thermostat was maintained within an accuracy of ± 2° C. The corrosion rates (C R), inhibition efficiencies (I E) and surface coverage (θ) of different concentrations of the inhibitors were calculated using the following equations: –

$$\text{Corrosion rate (C.R.) (mmpy)} = \frac{87.6 \text{ X } w}{d \text{ X } a \text{ X } t}$$

$$I\,E\,(\%) = \frac{\text{uninhibited corrosion rate} - \text{inhibited corrosion rate}}{\text{uninhibited corrosion rate}} \text{ X } 100$$

$$\theta = \frac{\text{uninhibited corrosion rate-inhibited corrosion rate}}{\text{uninhibited corrosion rate}}$$

Where, **w** = weight loss (in grams)

d = density of mild steel (7.86 cm^3)

a = area of the sample (in cm^2)

t = time of immersion (in hours)

2.8.2 POTENTIODYNAMIC POLARIZATION STUDIES

Polarization curves were recorded potentiodynamically using an EG & G PARC model 173 potentiostat / galvanostat, a model 175 universal programmer and a model RE 0089 X - Y recorder at 35 ± 2°C using the ASTM standards [14]. The cell assembly consists of a mild steel as working electrode, a platinum as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The working electrode of 1 cm x 1 cm with a tag of 5 cm were cut from the mild steel sheet and polished with the 1 / 0 to 4 / 0 grade of emery papers. The specimens were then thoroughly washed with distilled water and finally with trichloroethylene. Unwanted area of the electrode was coated with the lacquer to get a well defined working area of 1 cm^2. Various parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) and Tafel constant (b_a and b_c) were calculated from Tafel plot. All the potentials were measured against a saturated calomel electrode. The inhibition efficiencies were calculated using the following equations :–

$$I\,E\ (\%) = \frac{I_{ocorr} - I_{corr}}{I_{ocorr}} \times 100$$

Where, I_{ocorr} = Corrosion current density without inhibitor

I_{corr} = Corrosion current density with inhibitor

2.8.3 ELECTROCHEMICAL AC IMPEDANCE STUDIES

Electrochemical AC Impedance studies were carried out using an electrochemical impedance analyzer EG & G PARC system model M6310 with software M398 according to known procedure [15]. The cell assembly having mild steel as working electrode, platinum as auxiliary and reference electrodes was used. The block diagram of impedance set up is shown in Fig 2.0. The working electrodes were polished, degreased before each experiment and immersed in the test solution. Nyquist plots were drawn for the uninhibited and inhibited test solutions employing a frequency of 100 mHz to 10 KHz range. The real part (Z') and the imaginary part (Z") of the cell impedance were measured for various frequencies. The charge transfer resistance value (R_t) were determined by taking the difference in impedance values of high and low frequency intercepts of the real axis.

Various parameters such as double layer capacitance (C_{dl}), corrosion current density (I_{corr}) and Inhibition efficiency (I E) were calculated by using the following equations : –

$$C_{dl} = \frac{1}{2\,\pi\,f_{max}} \times \frac{1}{R_t}$$

$$I_{corr} = \frac{b_a \,.\, b_c}{2.3\ (b_a + b_c)} \times \frac{1}{R_t}$$

$$I\,E = \frac{1\,/\,R_{to} - 1\,/\,R_t}{1\,/\,R_{to}} \times 100$$

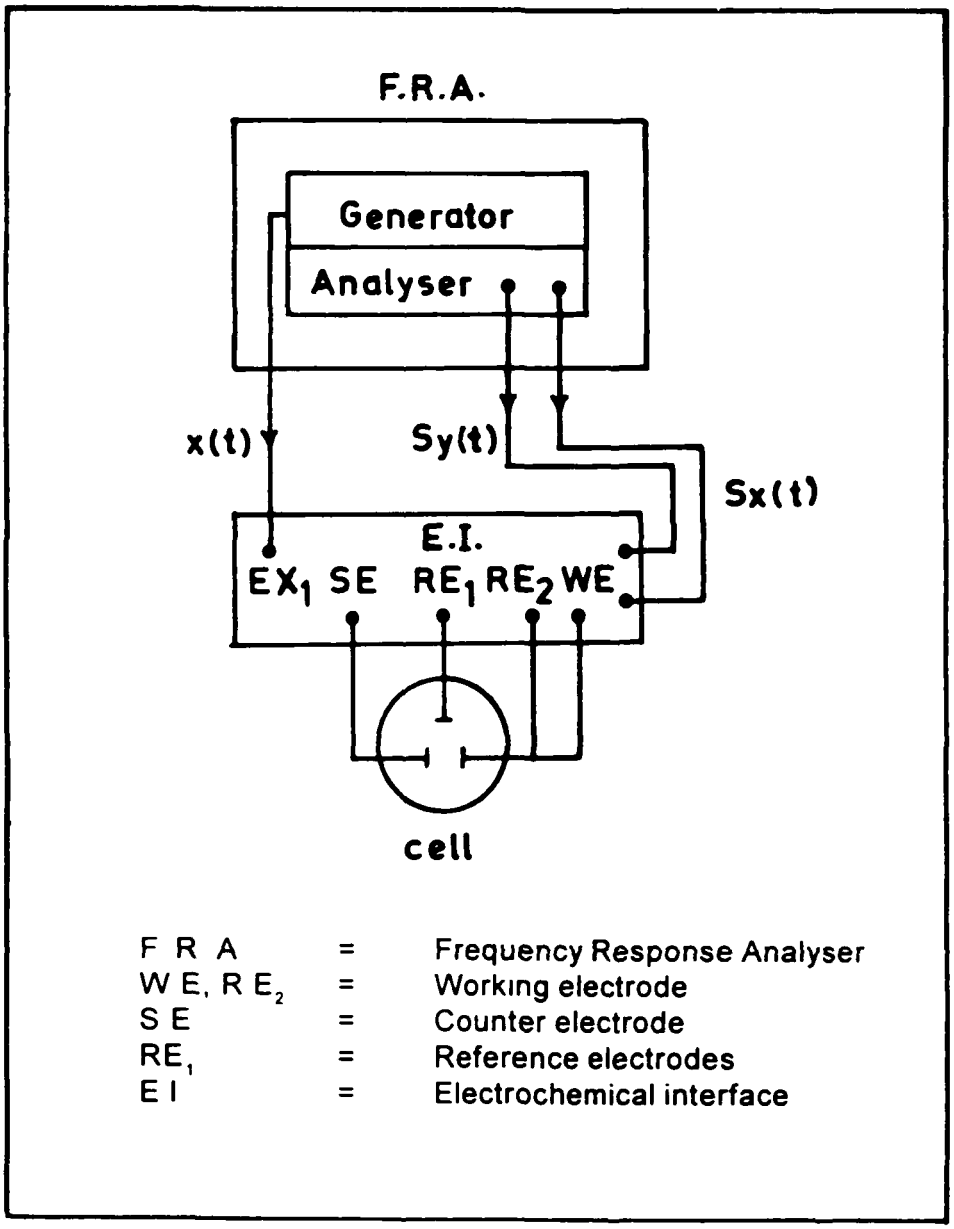


FIGURE 2.0 Block diagram of impedance setup

Where

f_{max} = the frequency at which the imaginary component of impedance (Z_{im} max) is maximum.

b_a & b_c = anodic & cathodic Tafel constants

R_{to} = charge transfer resistance without inhibitor

R_t = charge transfer resistance with inhibitor

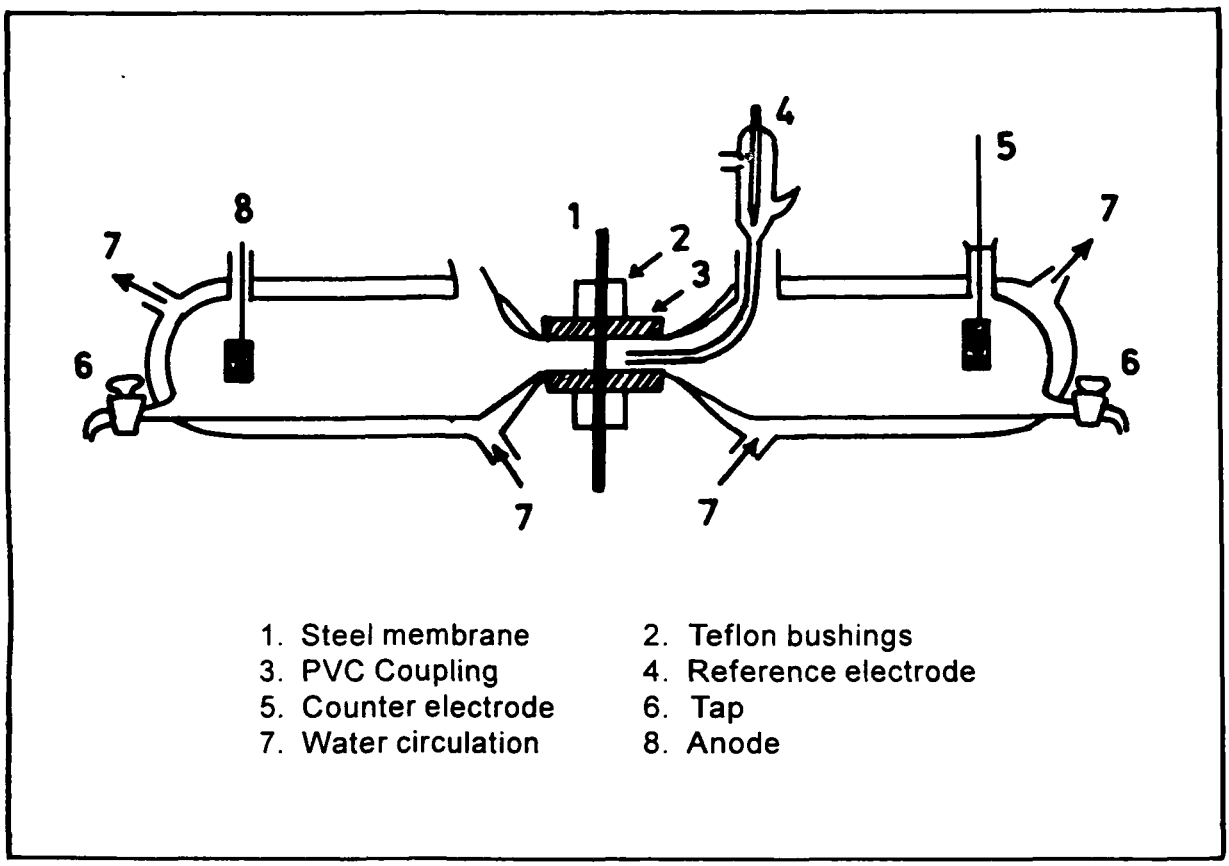
2.8.4 HYDROGEN PERMEATION STUDIES

Hydrogen Permeation Studies were carried out using an adaptation of the modified Devanathan and Stachurski's two compartment cell [14,15] and the hydrogen permeation curves were recorded using X - Y - T (Rikadenki) recorder at 30 ± 2°C. The complete permeation setup is shown in Fig. 2.1.

Mild steel specimens of the same composition with 1 cm^2 working area were used after mechanically polishing and degreasing with trichloroethylene. G R grade NaOH and BDH grade palladium chloride were used. Conductivity water was used for the solution preparation. In this method steel membrane functions as bipolar electrode in the cell. The cathodic side of the membrane remained in contact with experimental solution and the anodic side of the membrane was electroplated with a thin layer of palladium (palladised) by the following procedure:–

Specimens were polished, degreased, cathodically cleaned at the ambient temperature (35 ± 2°C) in the cleaning solution containing sodium hydroxide (35 gms / litre) and in sodium carbonate (25 gms / litre) at a current density of 150 $mAcm^{-2}$ for 5 minutes with mild steel as anode, then specimens were gently washed with double distilled water. The steel membrane was electroplated with a thin layer of palladium from the solution of the following composition:-

100 ml of double distilled water was heated to 80°C to this 1 gm of $PdCl_2$ was added followed by $NaNO_2$, until the $PdCl_2$ reacted completely to form a yellow solution of the complex $Na_2[Pd(NO_2)_4]$. This complex salt solution was added to 1000 c.c. of 0.2 M NaOH solution prepared from double distilled water and AR grade NaOH pallets.



1. Steel membrane
2. Teflon bushings
3. PVC Coupling
4. Reference electrode
5. Counter electrode
6. Tap
7. Water circulation
8. Anode

FIGURE 2.1 Complete Permeation cell setup

The steel membrane was fitted in between the PVC disc clamp with teflon bushing (Fig 2.1), with a circular 1 cm^2 exposed area and this prepared solution was filled in cell assembly. After coating palladium solution is removed at low current density 100 μAcm^{-2} this solution gave a bright coherent yellow coloured coating of palladium on the steel membrane for 90 minutes duration using platinum as the anode.

2.8.4.1 MEASUREMENT OF PERMEATION CURRENT

The palladised steel membrane inserted in between clamp was fitted in two compartment cell assembly tightly fitted without any leakage of the solution. The compartment facing palladium plated side was filled with 0.2 N NaOH solutions which was pre - electrolysed for a period of 12 hours at a current of 2.5 mA. A Hg / HgO / 0.2 N NaOH reference electrode and platinum counter electrode were introduced to complete the circuit.

The cell was connected to a potentiostat (Wenking model : POS 73) and a constant potential of -300 mv was applied to the specimen. It has been reported by Srinivasan et.al. [16] that – 300 mv is the most suitable potential for ionizing the diffused hydrogen rapidly and efficiently at Pd / 0.2 N NaOH interface. Water was circulated through the double wall of the cell and the temperature was maintained at 35 ± 2°C. The potential was maintained steady and constant till a steady background current was obtained. In all these studies a residual current of very low value was obtained. After reaching the steady background current at the anode compartment, the test solution (acid or inhibited solution) was introduced into the cathode compartment and allowed to corrode the steel membrane. The permeation current was simultaneously recorded on the recorder.

2.8.5 AUGER ELECTRON SPECTROSCOPY

Auger electron spectroscopy is one of the most popular and powerful technique to analyze the chemical species within the outermost surface layers of the specimens. The presence of different elements species can be distinguished by their characteristic peaks in the auger spectra [17]. The auger analysis of the samples were accomplished

by using an auger electron spectroscope (VARIAN CMA VT - 112 model), specimens were polished using different grades of emery papers and then dipped in the inhibited acid solution containing different concentrations of the inhibitors for 3 hours, rinsed with triple distilled water and dried at room temperature. The specimens were fixed onto a sample holder and introduced into a fast - entry air lock (FEAL) chamber maintained at a vacuum level of 10^{-11} torr (1.33 X 10^{-9} pa). After degassing the specimens were transferred into the preparation chamber, Specimens again were kept for long enough to facilitate further degassing. The specimens then were introduced into the analyzer chamber. The area of interest was selected with the help of a scanning electron microscope (SEM) attached to the instrument and excited with a 3 Kev electron beam. The depth of the resolution was 2 Å to 20 Å. The appearance of peaks of different elements at specific ev confirms the presence of that element on the adsorbed surface of mild steel.

The atomic concentration of the element (X) present on the adsorbed layer is calculated by using the relation: –

$$C_X = \frac{I_X}{I_{Ag} \cdot S_X \cdot D_X}$$

Where I_X = peak - to - peak amplitude of the element X from the test specimen.

I_{Ag} = peak - to - peak amplitude of the Ag standard.

D_X = relative scale factor between the spectra for the test specimen and silver.

S_X = relative sensitivity between any element X and silver.

2.8.6 SCANNING ELECTRON MICROSCOPY

To study the morphology of corroded surface of the specimen and formation of film at various stages in presence and absence of inhibitors Scanning electron microscope (SEM), model JEOL JSM 840, SM was used.

The specimens were polished with emery papers of different grades and washed with double distilled water and trichloroethylene. These specimens were then exposed to testing corrodent for 3 hours. After this these specimens were thoroughly

washed with double distilled water before putting them on the slide. These mild steel samples were cutted according to the size of the sample holder, fixed on the stub with carbon paste, coated with gold and then viewed. The micrographs have been taken from that portion of the specimen from where better information was obtained. They were photographed at the appropriate magnification.

To understand the morphology of the steel surface in absence and presence of inhibitors the following cases have been examined :–

1. Polished mild steel specimens
2. Mild steel specimen dipped in 1N HCl
3. Mild steel specimen dipped in 1N HCl containing optimum concentration of inhibitors.

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CHAPTER 3

RESULTS & DISCUSSION

SECTION 1

MACROCYCLIC COMPOUNDS AS CORROSION INHIBITORS

A macrocycle is defined as a cyclic compound having nine or more atomic members with three or more ligating atoms [1]. Macrocyclic complexes such as haemoglobin, chlorophyll and vitamin B_{12} play the vital role in living organism [2 - 7]. The synthesis, characterization and applications of macrocyclic compounds is an active field of research for co - ordination chemists.

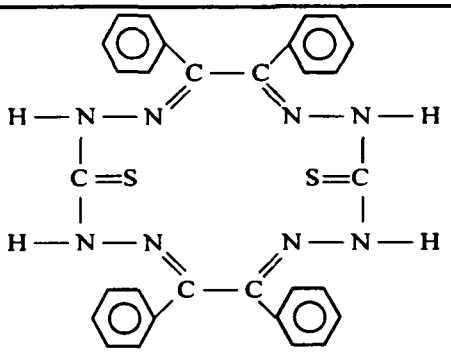
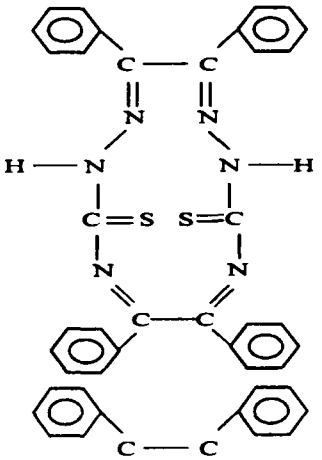
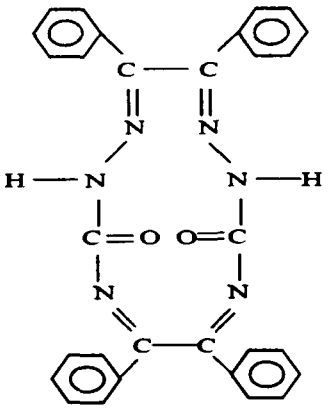
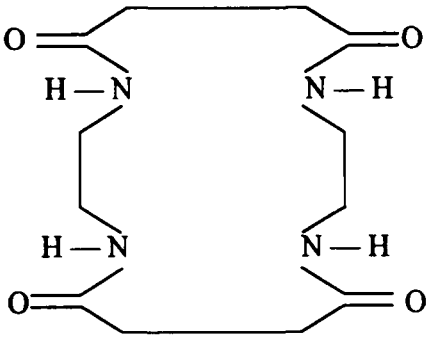
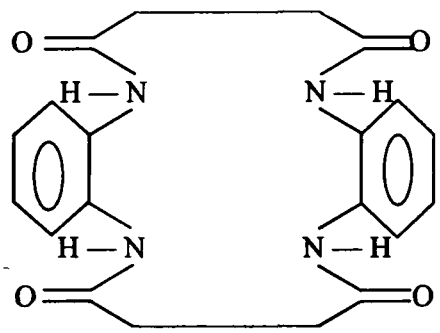
The corrosion inhibiting action of the macrocyclic compounds is attributed to their fascinating molecular structure. These molecules are adsorbed on the metal surface through π electrons or non - bonding electrons present in these molecules. In addition to these structural features planarity of these molecules further facilitates the formation of strong bond between metal and macrocyclic molecules [8, 9]. These observations led to the synthesis and evaluation of a few macrocyclic compounds as corrosion inhibitors [10 - 15].

This section deals with the investigation of some macrocyclic compounds on mild steel corrosion in acidic solutions (HCl and H_2SO_4). The molecular structures and names of the macrocyclic compounds are given in Table 3.1.1. Weight loss, Potentiodynamic polarization, electrochemical impedance, hydrogen permeation, auger electron spectroscopy and scanning electron microscopy have been used to study the corrosion inhibition effect of these inhibitors.

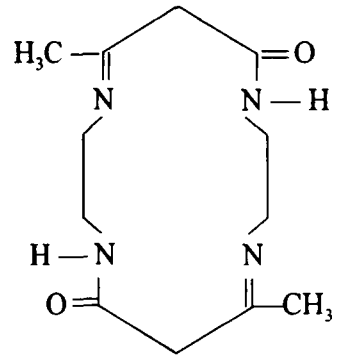
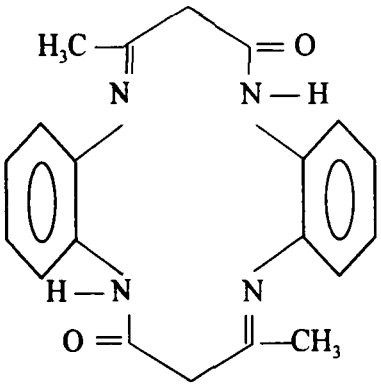
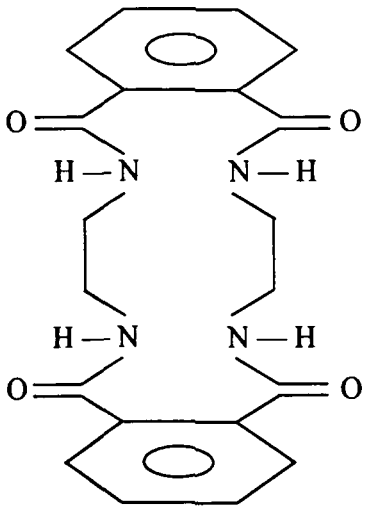
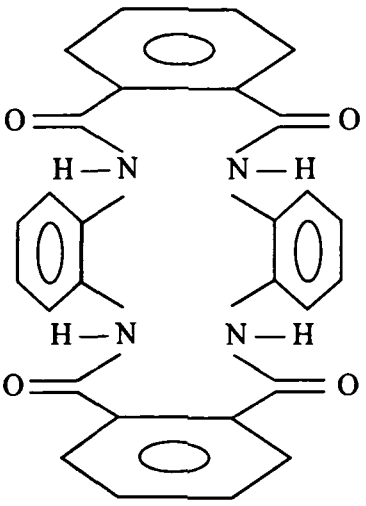
3.1.1 WEIGHT LOSS STUDIES

The weight loss measurements were conducted in 1N, 3N and 5N HCl at 40° C temperature for 3 hours. Corrosion inhibition tests were also carried out in 1N HCl and 1N H_2SO_4 for selected compounds (BMOAT, MOAT ,OAH, BOAH, DBOAD and TBOAD) at room temperature for 3 hours. The effect of temperature (40 - 70°) and immersion period (24 - 96 hours) was also studied on the inhibition efficiencies of these compound.The values of inhibition efficiency (I E) and corrosion rate (CR) for macrocyclic compounds (PTAT, PTAB and POAB) in 1N, 3N and 5N HCl are given in Table 3.1.2. The maximum inhibition efficiency of these compounds was found at 500, 700 and 2000 ppm in 1N, 3N and 5N HCl respectively. The influence of

TABLE 3.1.1 NAME AND STRUCTURAL FORMULAE OF THE INHIBITORS USED

S.No.	STRUCTURAL FORMULA	DESIGNATION AND ABBRIVIATION
1		Tetraphenyl-dithia-octaaza-cyclotetradecane hexaene (PTAT)
2		Tetraphenyl-dithia-hexaaza-cyclobidecane hexaene (PTAB)
3		Tetraphenyl-dioxo-hexaaza-cyclobidecane hexaene (POAB)
4		2,5,10,13-tetraoxo-1,6,9,14-tetraazacyclohexadecane (OAH)
5		7,8:15,16-dibenzo-2,5,10,13-tetraoxo-1,6,9,14 -tetraazacyclo-hexadecane (BOAH)

Contd.....

S.No.	STRUCTURAL FORMULA	D ESIGNATION AND ABBRIVIATION
6		7,14-dimethyl-5,12-dioxo-1,4,8,11-tetaazacyclotetradeca-1,7-diene (MOAT)
7		2,3:9,10-dibenzo-7,14-dimethyl-5,12-dioxo-1,4,8,11-tetraaza-cyclotetradeca-1,7-diene (BMOAT)
8		3,4:11,12-dibenzo 2,5,10,13-tetraoxo-1,6,9,14-tetraazacy-clohexadecane (DBOAD)
9		3,4:7,8:11,12:15,16-tetrabenzo-2,5,10,13-tetraoxo-1,6,9,14-tetraazacyclohexadecane (TBOAD)

inhibitor concentration on I E of macrocyclic compounds in 1N HCl has been illustrated in Figure 3.1.1 (a). It is evident that I E increases on increasing the concentration of inhibitor and reaches maximum at optimum concentration of 500 ppm.The inhibition efficiencies of all of the three investigated macrocyclic compounds followed the order :—

PTAT > PTAB > POAB

The difference in the inhibitive action of three macrocyclic compounds can be explained on the basis of their molecular structures. PTAT contains 10 heteroatoms (8 nitrogen and 2 sulphur) as reactive centres through which it adsorbs on the metal surface and gives an I E of 83 % while PTAB and POAB contain only 8 heteroatoms as reactive centers. Since compounds containing both nitrogen and sulphur atoms are reported to be better inhibitors than those containing nitrogen and oxygen atoms [16]. Hence PTAB (6 nitrogen and 2 sulphur atoms) gives better performance as corrosion inhibitor than POAB (6 nitrogen and 2 oxygen atoms).

The influence of acid concentration, temperature and immersion time on inhibition efficiency of these compounds has been shown in Figure 3.1.1 (b - d). It is seen that increase of acid concentration from 1N to 3N does not cause any significant change in I E values. However, I E for all the macrocyclic compounds decreases in 5N HCl due to increase in the aggresivity of HCl. I E of all the investigated compounds increases from 40 - 60°C, but above 60°C I E decreases due to the desorption of inhibitors from the metal surface. The effect of immersion period on inhibition efficiencies has been shown in Figure 3.1.1 (d). It is obvious that I E increases with immersion time. The increase in I E with time may be attributed to the formation of a barrier film which prevents the attack of acid on metal surface.

The corrosion parameters obtained from the weight loss measurement for different concentrations of macrocyclic compounds (TBOAD, DBOAD, BMOAT, MOAT, BOAH and OAH) in 1N HCl and 1N H_2SO_4 are given in Table 3.1.3. It is seen from the table that I E increases with increase in inhibitor concentration for all the compounds and reaches maximum at the optimum concentration of 1000 ppm in both acids. The effect of inhibitor concentration on I E in 1N HCl and 1N H_2SO_4 has

Table 3.1.2 - Corrosion parameters obtained from weight loss measurements for mild steel in 1N, 3N and 5N HCl containing different concentrations of macrocyclic compounds at 40°C for 3 hours.

Inhi. Conc.(PPM)	PTAT		PTAB		POAB	
	I E (%)	C R (mmpy)	I E (%)	C R (mmpy)	I E (%)	C R (mmpy)
1 N HCl	--	16.81	--	16.81	--	16.81
25	63.80	6.08	52.40	7.98	45.00	9.24
50	67.40	5.47	57.40	7.15	53.30	7.84
100	74.50	4.27	64.00	6.03	61.30	6.50
200	76.80	3.90	71.50	4.78	68.50	5.29
300	79.50	3.43	76.80	3.90	74.30	4.31
400	80.10	3.34	79.00	3.52	75.10	4.17
500	81.40	3.11	79.20	3.48	78.10	3.66
3 N HCl	--	57.76	--	57.76	--	57.76
100	64.30	20.57	46.60	31.19	44.01	32.32
200	79.50	11.84	54.00	26.56	53.00	27.11
300	82.40	10.16	61.00	22.47	60.20	22.94
400	84.20	9.10	66.10	19.55	61.40	22.29
500	87.70	7.10	66.30	19.45	67.70	18.66
600	88.90	6.40	71.10	16.67	70.50	17.04
700	90.10	5.66	74.90	14.48	72.00	16.16
5 N HCl	--	139.49	--	139.49	--	139.49
500	52.20	66.59	32.60	93.94	30.00	97.56
700	57.80	58.74	40.00	83.58	36.00	89.20
1000	70.20	41.56	48.30	72.11	45.10	76.48
1500	80.40	27.25	59.90	55.86	55.10	62.36
2000	84.10	22.15	62.50	52.28	61.40	53.72

Table 3.1.3 -Corrosion parameters obtained from weight loss measurements for mild steel in 1N HCl and H_2SO_4 containing different concentrations of macrocyclic compounds at 35°C for 3 hours.

Inhi. Conc. (ppm)	1N HCl		1N H_2SO_4	
	I E (%)	CR (mmpy)	I E (%)	CR (mmpy)
BLANK	--	12.40	--	19.10
TBOAD				
100	78.28	2.70	77.43	4.30
200	82.02	2.20	81.31	3.60
300	86.14	1.70	82.28	3.40
400	90.26	1.20	83.01	3.30
500	93.63	0.80	84.95	2.90
1000	96.25	0.50	88.65	2.60
DBOAD				
100	72.76	3.40	73.30	5.10
200	77.90	2.70	77.67	4.20
300	82.02	2.20	81.31	3.60
400	87.27	1.60	82.28	3.40
500	89.14	1.30	83.06	2.00
1000	94.01	0.70	87.14	2.50
BMOAT				
100	64.42	4.40	30.58	13.30
200	77.52	2.80	37.14	11.20
300	82.77	2.10	40.29	11.80
400	85.02	1.90	50.00	9.40
500	90.26	1.20	51.46	9.10
1000	98.58	0.20	65.29	6.50

Contd------

Inhi. Conc. (ppm)	1N HCl		1N H_2SO_4	
	I E (%)	CR (mmpy)	I E (%)	CR (mmpy)
BLANK	--	12.40	--	19.10
MOAT				
100	48.12	7.20	20.39	15.20
200	62.92	4.60	28.39	13.70
300	64.79	4.40	31.16	13.10
400	68.16	3.90	40.53	11.40
500	71.91	3.50	42.48	11.00
1000	84.64	1.90	54.16	8.80
BOAH				
100	56.18	5.40	23.01	14.70
200	66.29	4.20	32.77	12.60
300	70.78	3.60	35.90	12.30
400	74.16	3.20	41.26	11.20
500	74.91	3.10	46.36	10.30
1000	88.01	1.50	59.71	7.70
OAH				
100	47.56	6.50	10.92	17.00
200	53.18	5.80	18.69	15.60
300	63.30	4.60	21.12	15.10
400	68.54	3.90	25.24	14.30
500	68.91	3.80	27.18	13.90
1000	83.52	2.00	31.31	13.10

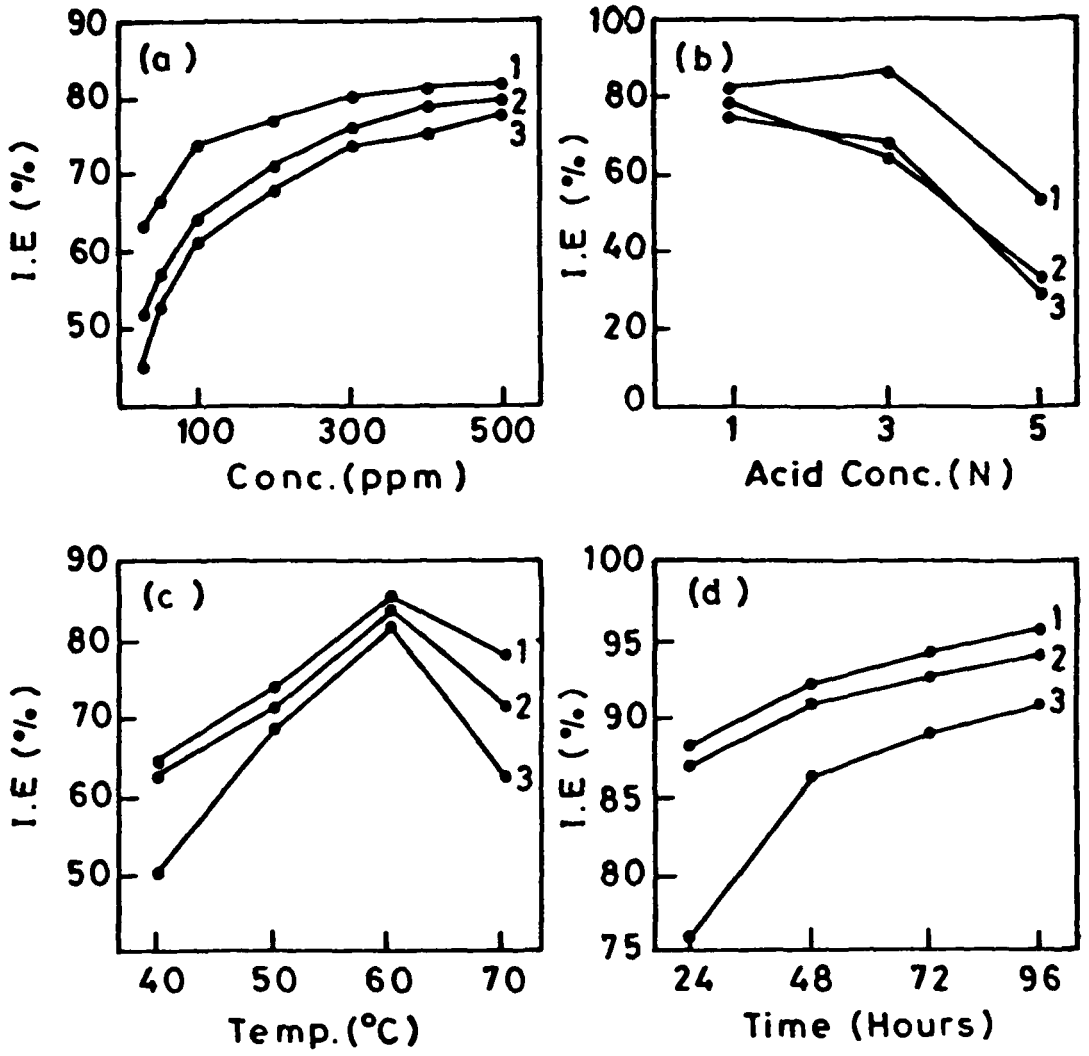


FIGURE 3.1.1 Variation of inhibition efficiency with –

(a) Inhibitor concentration (ppm) at 40°C in 1N HCl

(b) Concentration (N) of HCl cotaining 500 PPM of inhibitor at 40°C

(c) Temp (°C) in 1 N HCl cotaining 500 PPM of inhibitor

(d) Immersion time (hours) at room temp 35 ± 2°C in 1 N HCl containing 500 ppm concentration of inhibitors

1 PTAT 2 PTAB 3 POAB

been illustrated in Figure 3.1.2 (a, b).

The superior corrosion inhibitive behavior of TBOAD than that of DBOAD may be attributed to the presence of four aromatic rings. This facilitates greater adsorption of TBOAD on the metal surface as compared to DBOAD, which has only two rings.

The better performance of BMOAT and BOAH as corrosion inhibitor than that of MOAT and OAH is attributed to the presence of aromatic rings containing π electrons which facilitates greater adsorption of BMOAT and BOAH on the metal surface. On the other hand MOAT and OAH show lesser inhibition efficiency due to lack of the aromatic rings in these macrocyclic compounds. Desai et. al. have also reported that the condensation products derived from the aromatic amines and carbonyl compounds give better inhibition efficiency than those derived from ethylene diamine and carbonyls [17]. Thus the order of inhibition efficiencies based on the molecular structure of the compounds (4 - 9) may be represented as below :—

TBOAD > DBOAD > BMOAT > BOAH > MOAT > OAH

Figures 3.1.2 (c, d) show the effect of temperature on inhibition efficiencies. It is seen that I E decreases with the increase in temperature because at high temperature desorption of inhibitor molecules takes place from the metal surface at a faster rate [18]. Figures 3.1.2 (e, f) show the variation of inhibition efficiency with immersion period. The increase in I E with increasing immersion time may be attributed to the formation of a barrier film which prevents the attack of acid on the metal surface.

A noteworthy feature of the investigation is that all compounds (4 - 9) under study show more inhibition efficiency in 1N HCl than in 1N H_2SO_4. This can be explained by the fact that specific adsorption of the anions depends on the polarizability and the size of the ions. Heavily hydrated ions of smaller size are less specifically adsorbed than larger ions which are devoid of hydration sheaths. It appears that the loss of hydration sheath at least in the direction of the metal surface is a necessary condition for specific adsorption [19]. The number of primary water molecules surrounding each ion (s) is given below [20]: —

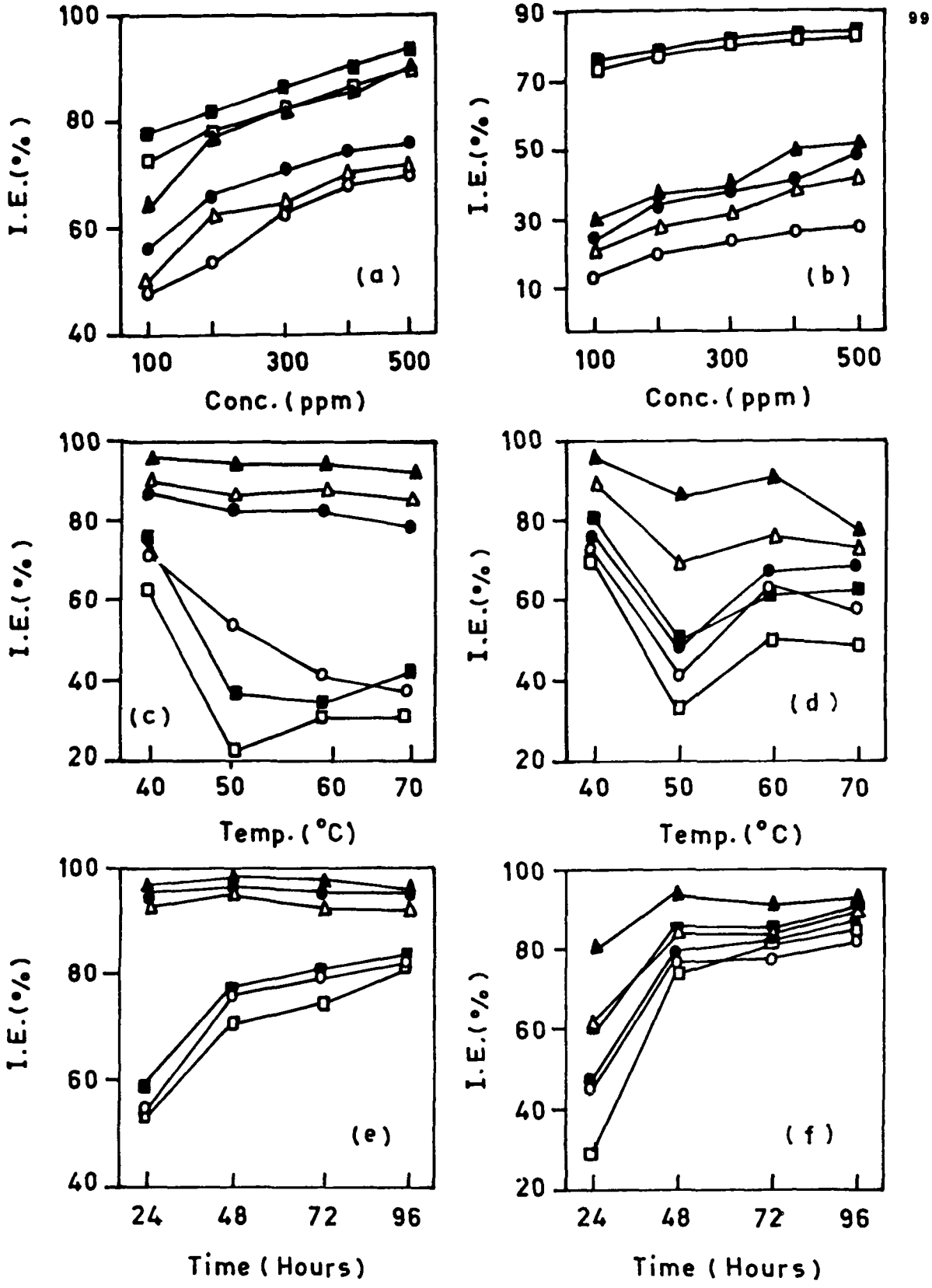


FIGURE 3.1.2 Variation of inhibition efficiency with :–

1. Inhibitor concentration (ppm)	(a) in 1N HCl	(b) in H_2SO_4
2. Temp. (°C)	(c) in 1N HCl	(d) in H_2SO_4
3. Immersion time (hours)	(e) in 1N HCl	(f) in H_2SO_4

■ TBOAD, □ DBOAD, ▲ BMOAT, △ MOAT, ● BOAH, ○ OAH

Ions	No. of primary water molecules (n)
I^-	0.3
Br^-	1.0
Cl^-	1.6
F^-	3.9
SO_4^{--}	11.0

Solvation number or primary hydration number is found to decrease with the increase in ionic radius and specific adsorption increases with ionic size and polarizability of the anion. In this respect chloride ions are more specifically adsorbed than sulphate ions. Stronger adsorption of chloride ions on the metal surface favours more adsorption of organic molecules as cations on the metal surface leading to enhanced inhibition. Lesser specific adsorption of sulphate ions leads to lesser adsorption of organic molecules and less inhibition.

According to Frumkin [21] and Iofa [22], the increased adsorption of organic cations thereby more inhibition can be attributed to changes of surface charge on the metal in the presence of halide ions. The metal at the open circuit potential, becomes negatively charged and cations are attracted by electrostatic forces to the metal surface. The extent of specific adsorption is more in the case of chloride ion, leading to more inhibition in this case. According to Iofa and Tomashova [23], the enhanced corrosion inhibition in HCl may be due to the fact that anion being specifically adsorbed, creates an excess negative charge towards the solution phase and favours the adsorption of cations . Murakawa and Hackerman [24] are of the view that the strong adsorption of organic molecules on the iron surface occurs through the already adsorbed Cl^- or SO_4^{--} ions. If there are already adsorbed chloride or sulphate ions on the surfaces they will interfere with the adsorption of organic molecules. The lesser interference by SO_4^{--} than that by Cl^- ion is due to the weaker adsorbability and thereby lesser inhibition in H_2SO_4 solution. Granese

and Rosales have also shown better performance of inhibitors in HCl than in H_2SO_4 solution [25].

Table 3.1.4 and 3.1.5 give the values of I E for specific concentrations of inhibitors in combination with KI and show that I E increases with the addition of iodide ions for all of the compounds in the range of 10 - 40 % thereby suggesting that the enhanced inhibition efficiency of macrocyclic compounds caused by the addition of iodide ions is due to synergistic effect.

Table 3.1.4- Inhibition efficiencies of macrocyclic compounds obtained from weight loss measurements in absence and presence of KI

Inhi. Conc. (PPM)	KI Conc. (%)	IE (%)		
		PTAT	PTAB	POAB
1 N HCl				
100	--	74.50	64.00	61.30
100	0.02	82.60	79.60	76.40
300	--	79.50	76.80	74.30
300	0.02	85.60	80.90	78.40
3 N HCl				
200	--	79.50	54.00	53.00
200	0.05	86.70	74.90	70.30
500	--	87.70	66.30	67.70
500	0.05	90.80	76.70	78.70
5 N HCl				
500	--	52.20	32.60	30.00
500	0.10	76.40	60.90	57.80
1000	--	70.20	48.30	45.10
1000	0.10	80.60	66.00	60.00

Table 3.1.5- Inhibition efficiencies of macrocyclic compounds obtained from weight loss measurements in absence and presence of KI

1N HCl			1N H_2SO_4		
Inhi. Conc. (PPM)	KI Conc. (%)	IE (%)	Inhi. Conc. (PPM)	KI Conc. (%)	IE (%)
TBOAD					
200	--	82.02	300	--	82.28
200	0.02	92.90	300	0.03	97.10
400	--	90.26	500	--	84.95
400	0.02	97.00	500	0.03	99.80
DBOAD					
200	--	77.90	300	--	81.31
200	0.02	89.50	300	0.03	98.30
400	--	87.27	500	--	83.06
400	0.02	96.30	500	0.03	99.50
BMOAT					
300	--	82.77	400	--	50.00
300	0.02	97.38	400	0.03	98.30
400	--	85.02	500	--	51.46
400	0.02	98.88	500	0.03	99.27
MOAT					
300	--	64.79	400	--	40.53
300	0.02	95.88	400	0.03	83.90
400	--	68.16	500	--	42.48
400	0.02	98.50	500	0.03	87.86
BOAH					
300	--	70.78	400	--	41.26
300	0.02	97.75	400	0.03	96.36
400	--	74.16	500	--	46.36
400	0.02	99.25	500	0.03	98.54
OAH					
300	--	63.30	400	--	25.24
300	0.02	70.64	400	0.03	78.88
400	--	68.54	500	--	27.18
400	0.02	77.52	500	0.03	91.75

Table 3.1.6 gives the value of I E and C R obtained in the presence of different concentrations of macrocyclic compounds (1 - 3) in 5N HCl at 70° C for 30 minutes. All inhibitors have shown maximum I E at 2000 ppm concentration, no significant increase in I E is observed at 3000 ppm. The addition of KI (0.25 %) at 2000 ppm concentration of inhibitors enhanced the I E of macrocyclic compounds by more than 10 %.

Table 3.1.6- Corrosion parameters obtained from weight loss studies for mild steel in 5N HCl containing different concentrations of macrocyclic compounds with and without .025% KI at 70°C for 30 minutes.

Inhi. Conc. (PPM)	PTAT		PTAB		POAB	
	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)
5N HCl	--	1522.6	--	1522.6	--	1522.6
500	49.8	763.8	38.2	941.8	30.6	1056.1
1000	56.6	660.7	45.5	830.5	33.9	1006.6
1500	66.4	511.1	58.8	626.4	44.9	839.1
2000	68.9	479.5	60.9	595.6	55.3	680.3
3000	68.5	472.9	61.9	580.6	55.9	670.5
2000 + KI	83.3	253.9	72.7	415.5	69.9	458.6

3.1.1.1 ADSORPTION ISOTHERM

The dependance of adsorption of organic compounds on their concentration in the case of iron has been usually characterized by Langmuir, Temkin and Freundlisch isotherms. In the present study values of surface coverage (θ) were evaluated by using values of I E obtained from the weight loss data in 1 - 5 N HCl. Temkin isotherms were tested by plotting θ vs log C for all compounds. A straight line was obtained in all the cases [Figure 3.1.3 (a - c), 3.1.4 (a - b)], thereby clearly proving the fact that the adsorption of these compounds on the surface of mild steel obeys Temkin' s adsorption isotherm [26].

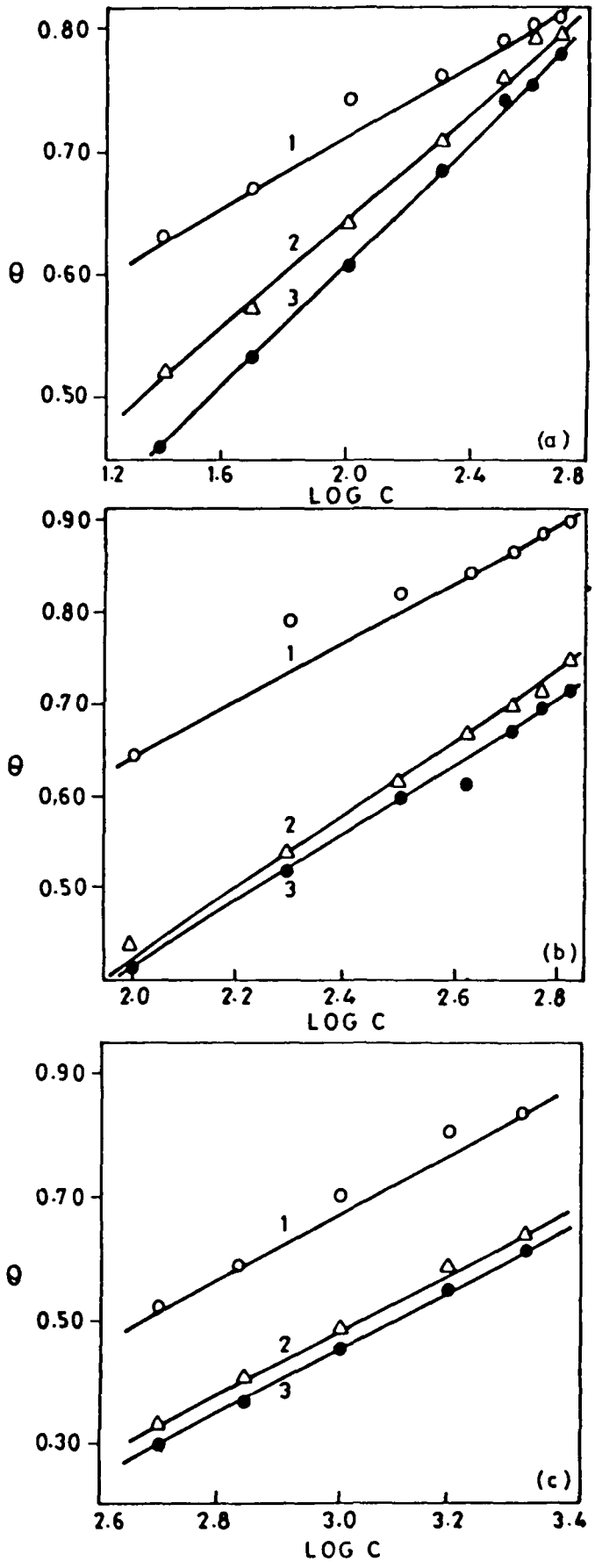


FIGURE 3.1.3 Temkin`s adsorption isotherm plots for mild steel in (a) 1 N (b) 3 N (c) 5 N HCl containing different concentrations of macrocyclic compounds :–
1. PTAT 2. PTAB 3. POAB

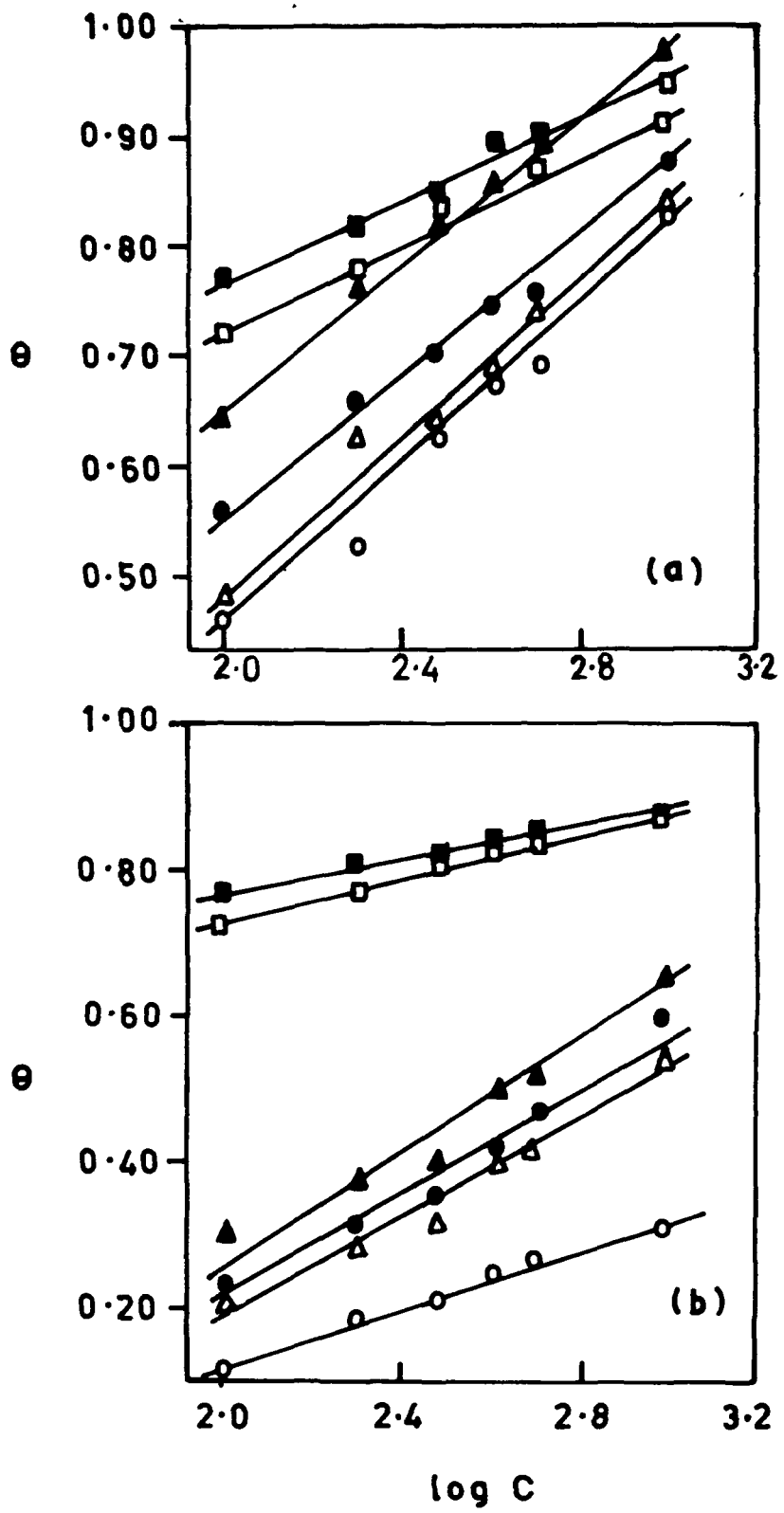


FIGURE 3.1.4 Temkin's adsorption isotherm plots for MS in (a) 1 N HCl (b) 1 N H_2SO_4 containing different concentrations of macrocyclic compounds :-
■ TBOAD, □ DBOAD, ▲BMOAT, △ MOAT, ● BOAH, ○ OAH

3.1.2 POTENTIODYNAMIC POLARIZATION STUDIES

The anodic and cathodic polarization behavior of mild steel in absence and presence of PTAT, PTAB and POAB in 1 - 5N HCl are shown in Figure 3.1.5 - 3.1.7 (a- d). Various corrosion parameters obtained from the polarization curves such as corrosion current density (I_{corr}), Corrosion potential (E_{corr}), Tafel slope constants (b_c and b_a) and inhibition efficiency (I E) of macrocyclic compounds PTAT, PTAB and POAB are given in Tables 3.1.7 - 3.1.9. These results show that all the compounds bring down I_{corr} value in all concentrations, but maximum decrease in I_{corr} value is obtained at 500, 700 and 2000 ppm in 1N, 3N and 5N HCl respectively. All of these three compounds show synergistic effect as shown by polarization studies, 1000 ppm + 0.1 % KI in 5N HCl give lower I_{corr} value. It is found that the addition of these compounds do not show significant shift of corrosion potential in 1 - 5 N HCl, showing the mixed nature of inhibitors.

Table 3.1.10 - 3.1.11 give the values of E_{corr}, I_{corr}, b_c, b_a and I E obtained for different concentrations of macrocyclic compounds TBOAD, DBOAD BMOAT, MOAT, BOAH and OAH in 1N HCl and 1N H_2SO_4. All compounds bring down the I_{corr} values at all concentrations in both acid, but the maximum decrease in I_{corr} values is observed at 1000 ppm concentration. A significant decrease in I_{corr} value is observed with 700 ppm inhibitor concentration and 0.25 % KI. The macrocyclic compounds BMOAT, MOAT , BOAH and OAH do not shift E_{corr} values in 1N HCl but bring about slight shift of E_{corr} value in 1N H_2SO_4 towards negative side, these observations clearly indicate that these compounds are mixed type inhibitors in HCl and predominantly cathodic in H_2SO_4 (Figure 3.1.8 a, b). The E_{corr} values obtained with TBOAD and DBOAD in 1N HCl and 1N H_2SO_4 do not show any significant change in E_{corr} value as well as in b_c and b_a values (Figure 3.1.8 c, d). This behavior suggests that these macrocyclic compounds (TBOAD and DBOAD) are mixed type inhibitors. Further improvement in their I E was observed on addition of 0.25 % of KI to acid solution containing 700 ppm of inhibitors.

Table 3.1.7- Potentiodynamic electrochemical parameters for mild steel in 1N HCl containing different concentrations of macrocyclic compounds at 35°C.

Inhi. Conc. (ppm)	I_{corr} (μAcm^{-2})	E_{corr} (mv)	b_c (mv dec^{-1})	b_a (mv dec^{-1})	IE (%)
1 N HCl	350	-554	130	60	–
PTAT					
50	86	-550	130	70	75.43
100	78	-552	126	54	77.71
300	82	-556	132	60	76.57
400	76	-558	130	50	78.29
500	74	-560	130	50	78.86
PTAB					
50	140	-564	118	54	60.00
100	110	-560	120	60	68.57
300	120	-562	120	60	65.71
400	100	-552	130	60	71.43
500	90	-562	130	60	74.29
POAB					
50	190	-564	110	50	45.71
100	160	-552	130	60	54.29
300	150	-562	130	60	57.14
400	135	-550	130	60	61.43
500	120	-560	130	60	65.71

Table 3.1.8- Potentiodynamic electrochemical parameters for mild steel in 3N HCl containing different concentrations of macrocyclic compounds at 35°C.

Inhi. Conc. (ppm)	I_{corr} (μAcm^{-2})	E_{corr} (mv)	b_c (mv dec^{-1})	b_a (mv dec^{-1})	IE (%)
3N HCl	1200	-568	130	70	--
PTAT					
100	374	-474	120	70	68.83
300	346	-578	120	60	71.17
500	176	-562	130	70	85.33
700	163	-565	120	60	86.42
PTAB					
100	467	-567	120	50	61.08
300	436	-566	130	60	63.67
500	360	-574	120	60	70.00
700	263	-573	130	60	78.08
POAB					
100	529	-566	130	60	55.92
300	462	-570	130	60	61.50
500	387	-574	120	60	67.75
700	356	-578	120	54	70.33

Table 3.1.9- Potentiodynamic electrochemical parameters for mild steel in 5N HCl containing different concentrations of macrocyclic compounds with and without (0.25%) KI at 35°C

Inhi. Conc. (ppm)	I_{corr} (μAcm^{-2})	E_{corr} (mv)	b_c (mv dec^{-1})	b_a (mv dec^{-1})	IE (%)
5N HCl	4000	-520	130	80	--
5N HCl + KI	580	-516	130	58	85.50
PTAT					
500	720	-528	120	60	82.00
700	550	-536	130	60	86.25
1000	340	-530	120	60	91.50
2000	330	-538	120	60	91.75
700 + KI	420	-540	115	55	89.50
1000+KI	328	-542	110	70	91.80
PTAB					
500	1000	-524	120	60	75.00
700	920	-524	110	50	77.00
1000	640	-526	120	60	84.00
2000	560	-524	110	60	86.00
700 + KI	460	-536	118	56	88.50
1000+KI	400	-540	120	58	90.00
POAB					
500	1800	-524	130	60	55.00
700	1200	-530	130	60	70.00
1000	1100	-526	120	60	72.50
2000	1000	-522	120	60	75.00
700 + KI	480	-520	120	60	88.00
1000+KI	440	-522	120	50	89.00

Table 3.1.10 - Potentiodynamic electrochemical parameters for mild steel in 1N HCl containing different concentrations of macrocyclic compounds with and without (0.25%) KIat 35°C

Inhi. Conc. (ppm)	I_{corr} (μAcm^{-2})	E_{corr} (mv)	b_c (mv dec^{-1})	b_a (mv dec^{-1})	IE (%)
1N HCl	350	-554	130	60	--
TBOAD					
200	160	-562	136	60	54.29
400	100	-560	140	66	71.43
1000	72	-554	135	65	79.43
400+KI	66	-552	140	70	81.14
DBOAD					
200	180	-566	138	68	48.57
400	120	-568	130	65	65.71
1000	96	-562	135	68	72.57
400+KI	98	-560	140	70	72.00
BMOAT					
100	180	-546	120	50	48.57
400	130	-532	125	55	62.86
1000	74	-526	120	50	78.86
400+KI	58	-534	125	45	83.43
MOAT					
100	190	-544	120	45	45.71
400	120	-530	130	60	65.71
1000	88	-522	125	50	74.86
400+KI	60	-534	130	60	82.86
BOAH					
100	170	-548	120	55	51.43
400	120	-544	120	60	65.71
1000	80	-530	124	66	77.14
400+KI	62	-528	132	68	82.29
OAH					
100	170	-548	120	55	51.43
400	120	-544	120	60	65.71
1000	80	-530	124	66	77.14
400+KI	62	-528	132	68	82.29

Table 3.1.11- Potentiodynamic electrochemical parameters for mild steel in 1N H_2SO_4 containing different concentrations of macrocyclic compounds with and without (0.25%) KI at 35°C.

Inhi. Conc. (ppm)	I_{corr} (μAcm^{-2})	E_{corr} (mv)	b_c (mv dec^{-1})	b_a (mv dec^{-1})	IE (%)
1N H_2SO_4	380	-580	110	55	--
TBOAD					
200	120	-592	124	60	68.42
500	82	-590	130	65	78.42
1000	56	-594	136	64	85.26
500+KI	66	-588	138	66	82.63
DBOAD					
200	120	-580	140	70	68.42
500	82	-584	138	68	78.42
1000	52	-578	136	60	86.32
500+KI	58	-586	130	60	84.74
BMOAT					
100	180	-596	110	58	52.63
500	120	-598	115	60	68.42
1000	55	-572	110	55	85.53
500+KI	37	-584	120	60	90.26
MOAT					
100	220	-584	110	50	42.11
500	140	-562	116	54	63.16
1000	94	-544	120	58	75.26
500+KI	68	-548	120	60	82.11
BOAH					
100	150	-582	125	60	60.53
500	130	-586	115	55	65.79
1000	76	-584	110	60	80.00
500+KI	55	-598	116	58	85.53
OAH					
100	200	-582	120	60	47.37
500	180	-586	110	50	52.63
1000	120	-576	120	55	68.42
500+KI	70	-600	115	58	81.58

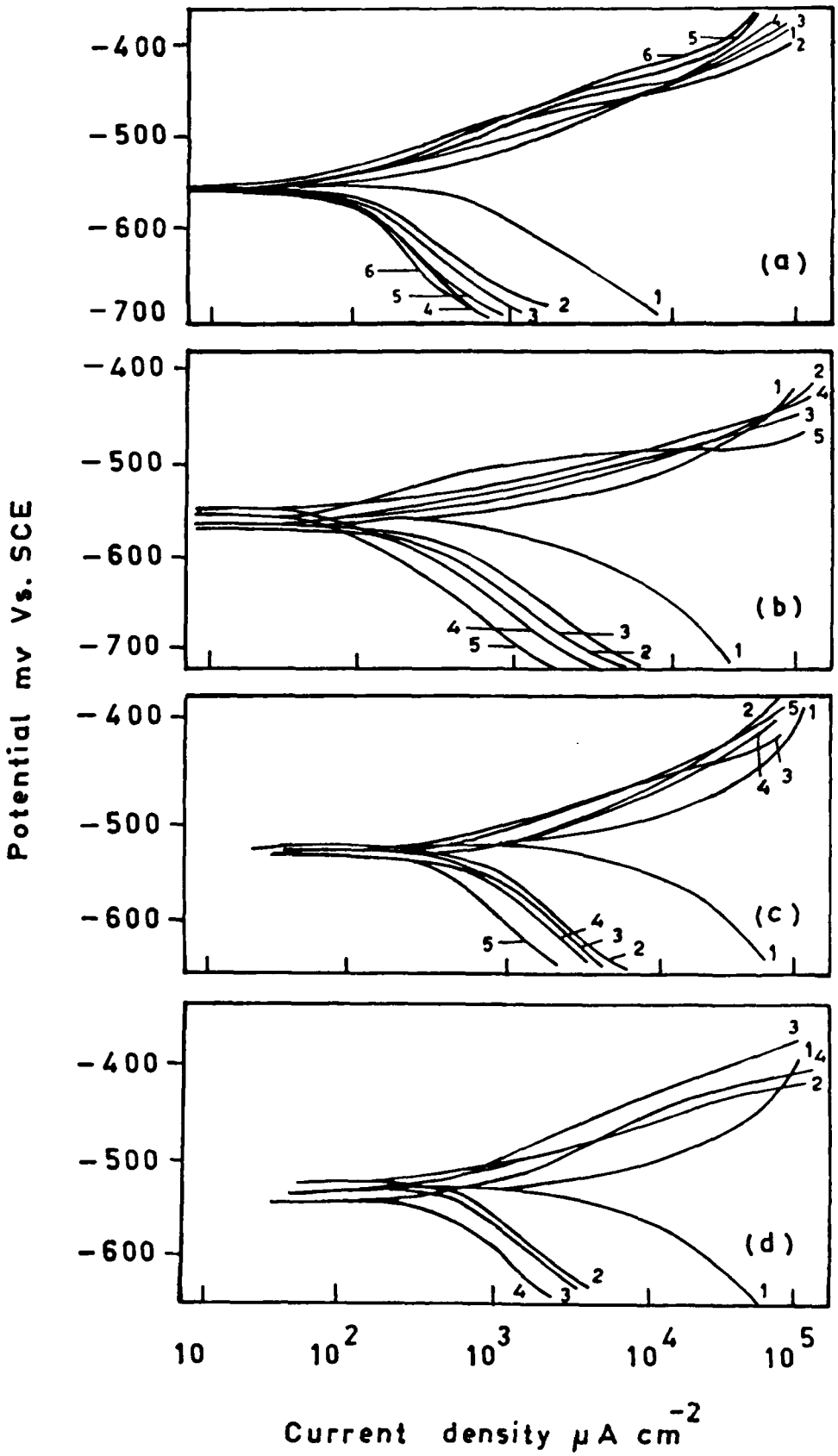


FIGURE 3.1.5 Potentiodynamic polarization curves for mild steel containing different concentrations of PTAT in : –

(a) 1N HCl : 1. Blank 2. 50 ppm 3. 100 ppm 4. 300 ppm 5. 400 ppm 6. 500 ppm
(b) 3N HCl : 1. Blank 2. 100 ppm 3. 300 ppm 4. 500 ppm 5. 700 ppm
(c) 5N HCl : 1. Blank 2. 300 ppm 3. 500 ppm 4. 700 ppm 5. 1000 ppm
(d) 5N HCl : 1. Blank 2. 5N HCl + KI 3. 500ppm + KI 4. 700 ppm + KI

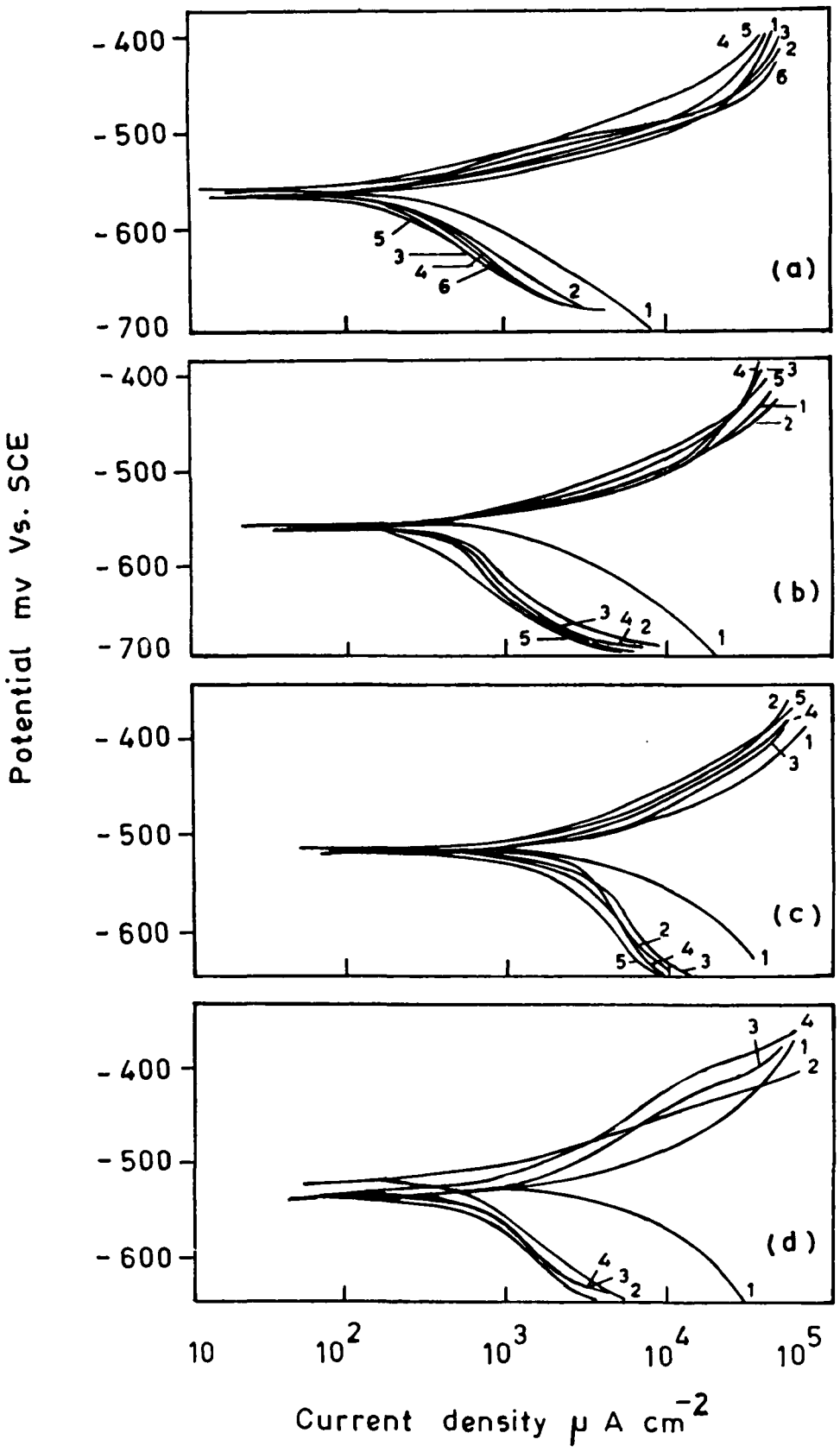


FIGURE 3.1.6 Potentiodynamic polarization curves for mild steel containing different concentrations of PTAB in : –

(a) 1N HCl : 1. Blank 2. 50 ppm 3. 100 ppm 4. 300 ppm 5. 400 ppm 6. 500 ppm
(b) 3N HCl : 1. Blank 2. 100 ppm 3. 300 ppm 4. 500 ppm 5. 700 ppm
(c) 5N HCl : 1. Blank 2. 300 ppm 3. 500 ppm 4. 700 ppm 5. 1000 ppm
(d) 5N HCl : 1. Blank 2. 5N HCl + KI 3. 500ppm + KI 4. 700 ppm + KI

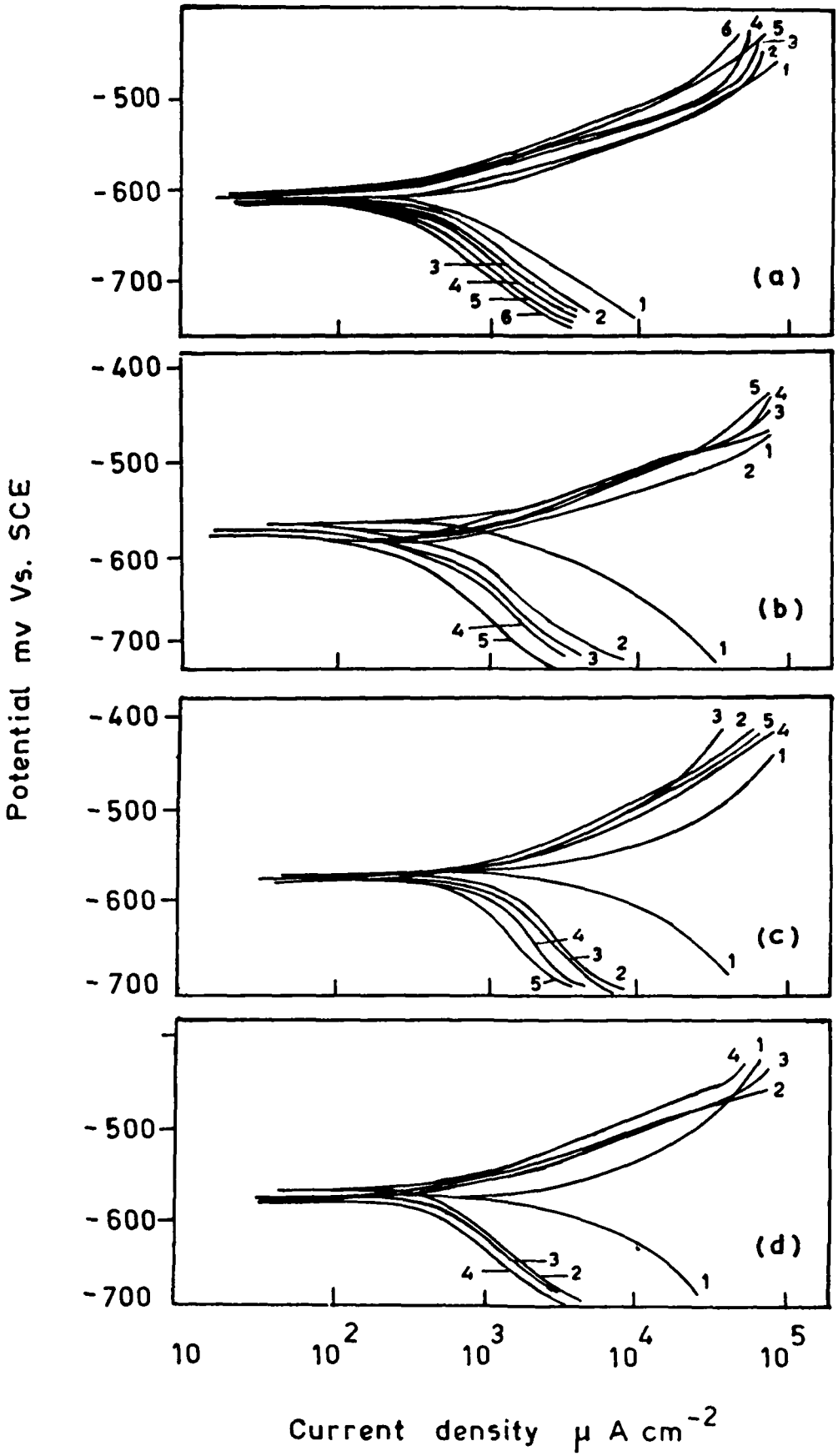


FIGURE 3.1.7 Potentiodynamic polarization curves for mild steel containing different concentrations of POAB in : –

(a) 1N HCl : 1. Blank 2. 50 ppm 3. 100 ppm 4. 300 ppm 5. 400 ppm 6. 500 ppm
(b) 3N HCl : 1. Blank 2. 100 ppm 3. 300 ppm 4. 500 ppm 5. 700 ppm
(c) 5N HCl : 1. Blank 2. 300 ppm 3. 500 ppm 4. 700 ppm 5. 1000 ppm
(d) 5N HCl : 1. Blank 2. 5N HCl + KI 3. 500ppm + KI 4. 700 ppm + KI

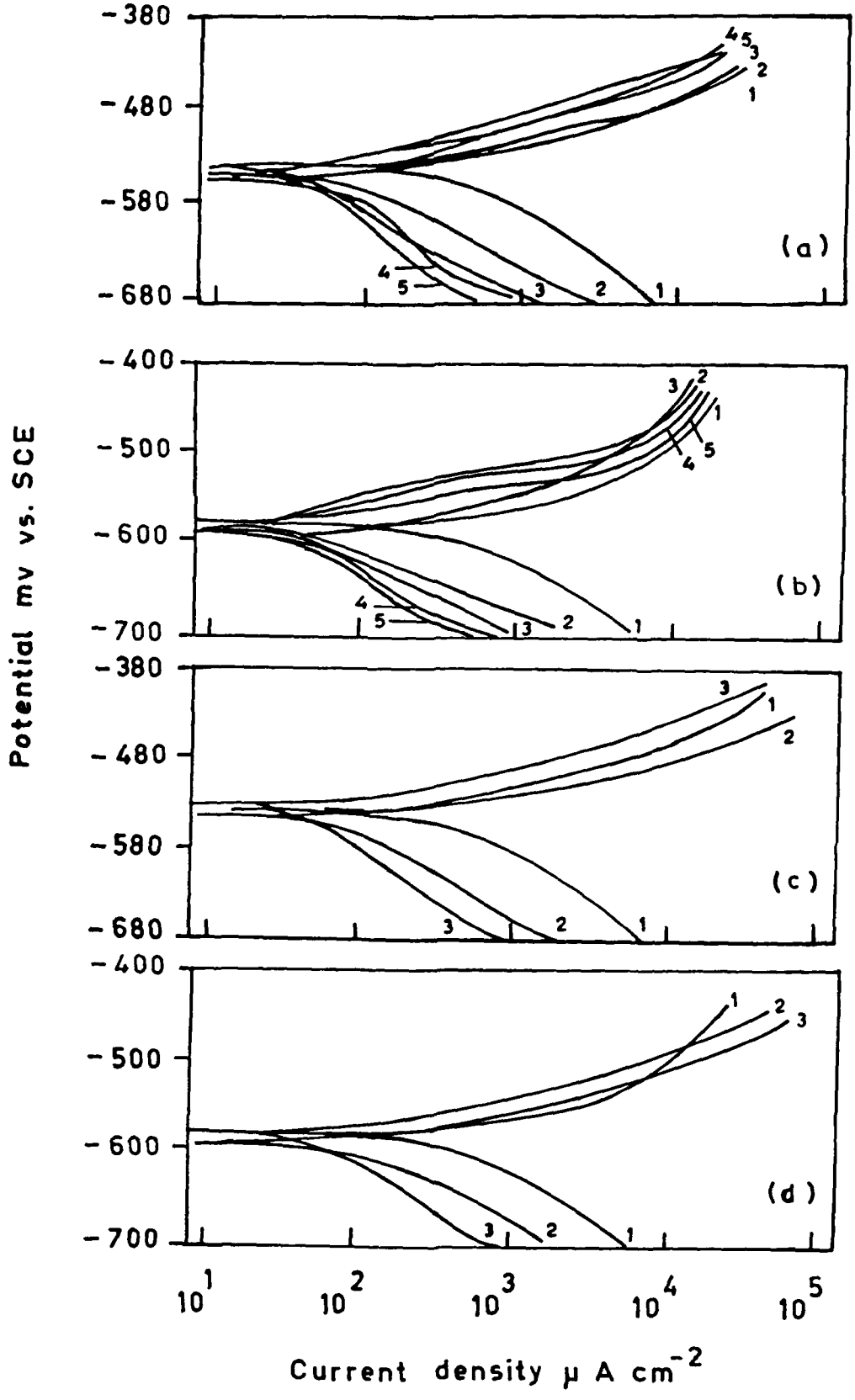


FIGURE 3.1.8 Potentiodynamic polarization curves for mild steel in absence and presence of 1000 ppm of macrocyclic compounds : –

(a) 1N HCl	: 1. Blank	2. OAH	3. BOAH	4. MOAT	5. BMOAT
(b) 1 N H_2SO_4	: 1. Blank	2. OAH	3. BOAH	4. MOAT	5. BMOAT
(c) 1N HCl	: 1. Blank	2 DBOAD	3. TBOAD		
(d) 1 N H_2SO_4	: 1. Blank	2. DBOAD	3. TBOAD		

3.1.3 ELECTROCHEMICAL IMPEDANCE STUDIES

Three macrocyclic compounds (PTAT, PTAB and POAB) have been investigated by AC impedance technique. Nyquist plots obtained from the impedance studies in 1N HCl containing optimum inhibitor concentration (500 ppm) are shown in Figure 3.1.9 (a - c) and various parameters such as charge transfer resistance (R_t), double layer capacitance (C_{dl}), corrosion current density (I_{corr}) and inhibition efficiency (I E) are given in Table 3.1.12.

The results clearly show that I_{corr} and C_{dl} values are less for inhibited systems as compared to those for uninhibited system and R_t values are higher for inhibited systems. These observations suggest that macrocyclic compounds inhibit corrosion by getting adsorbed on the metal surface, which increases the impedance (resistance) of the metal surface which in turn decreases I_{corr} as well as C_{dl} values.

Table 3.1.12 -Impedance data of mild steel in 1N HCl containing different concentrations of macrocyclic compounds.

SYSTEM	Inhi. Conc. (ppm)	R_t (Ω cm^2)	C_{dl} (μF cm^{-2})	I_{corr} (μ A cm^{-2})	I E (%)
1 N HCl	--	115	12832	155.2	--
PTAT	300	969	1623	18.5	88.13
	500	1156	1464	13.6	90.06
PTAB	300	746	2089	23.3	84.59
	500	962	1758	18.5	88.10
POAB	300	407	4338	43.8	71.79
	500	500	3384	35.6	77.10

3.1.4 HYDROGEN PERMEATION STUDIES

Macrocyclic compounds (PTAT and PTAB) have been investigated by hydrogen permeation study to evaluate the effect of inhibitors on the reduction of

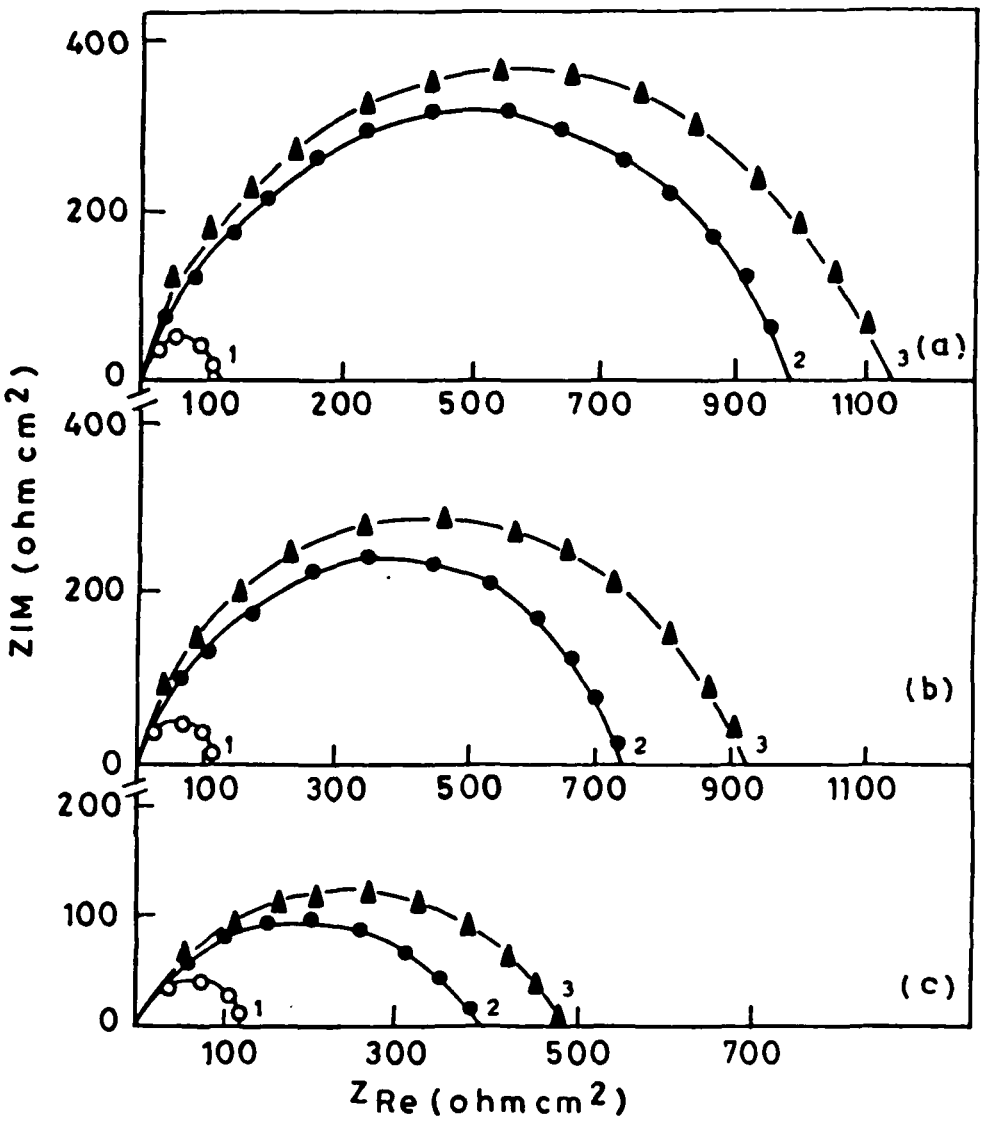


FIGURE 3.1.9 Nyquist plots for mild steel in 1N HCl in absence and presence of different concentrations of macrocyclic compounds :–

(a) PTAT (b) PTAB (c) POAB 1. Blank 2. 300 ppm 3. 500 ppm

hydrogen permeation. The values of permeation current and percentage reduction in presence of 500 ppm concentration of PTAT and PTAB in 1N HCl are given in Table 3.1.13.The permeation current vs time curves for mild steel in 1N HCl in absence and presence of inhibitors are shown in Figure 3.1.10. It is seen that both the compounds considerably reduce the hydrogen permeation current. The reduction of hydrogen permeation current may be attributed to the adsorption of these compounds on the mild steel surface, which prevents the entry of hydrogen into the metal.

Table 3.1.13 - Hydrogen permeation parameters for mild steel in 1N HCl containing 500 ppm of macrocyclic compounds at 35 ± 2°C

Inhi. Conc. (ppm)	Permeation current (μA)	Percent reduction (%)
1 N HCl	24	--
500 PTAT	17.3	27.9
500 PTAB	18.1	24.6

3.1.5 AUGER ELECTRON SPECTROSCOPY

The auger electron spectra for polished mild steel surface and mild steel exposed to a solution of PTAT and PTAT + K I are shown in Figure 3.1.11 (a - c). The appearance of peaks at 378 and 152 ev confirms the adsorption of PTAT on mild steel surface through nitrogen and sulphur atoms, similarly appearance of peaks at 511, 379 and 152 ev proves the presence of iodine, nitrogen and sulphur atoms respectively on mild steel inhibited with PTAT in presence of K I.

The values of atomic concentrations of different elements present on mild steel surface and in adsorbed inhibitor film on mild steel are given in Table 3.1.14. These data indicate the relative concentration of adsorbed species on the mild steel surface.

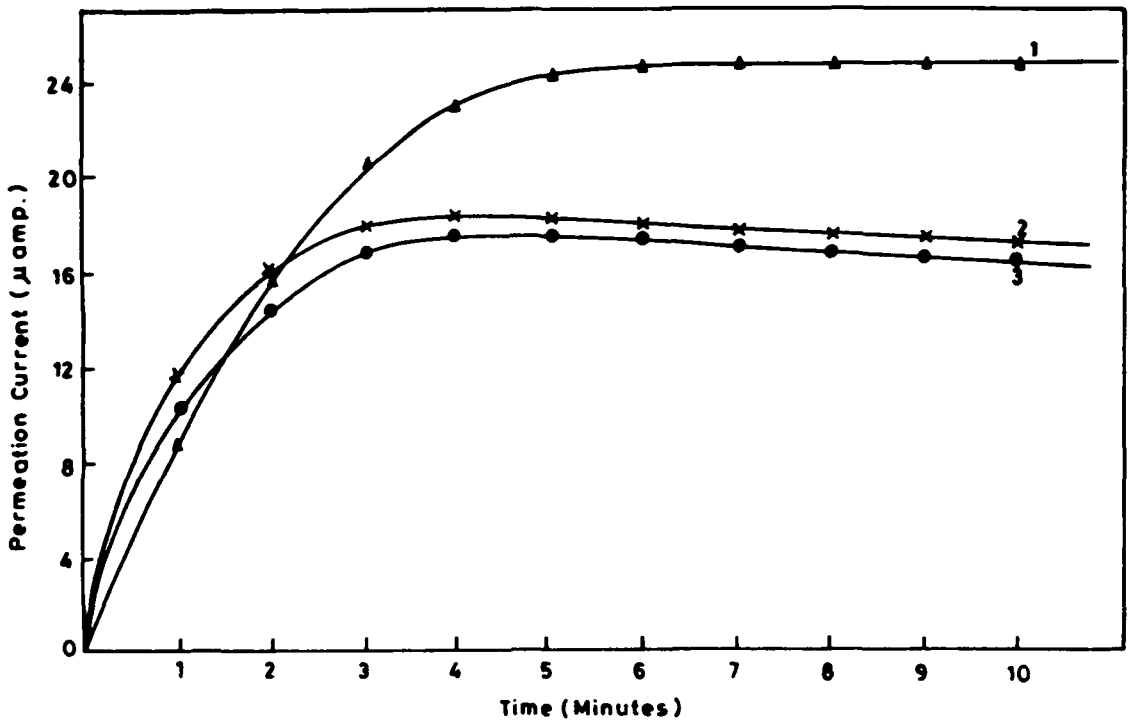


FIGURE 3.1.10 Hydrogen permeation curves for mild steel in 1N HCl in absence and presence of 500 PPM of macrocyclic inhibitors :–

1. Blank 2. PTAB 3. PTAT

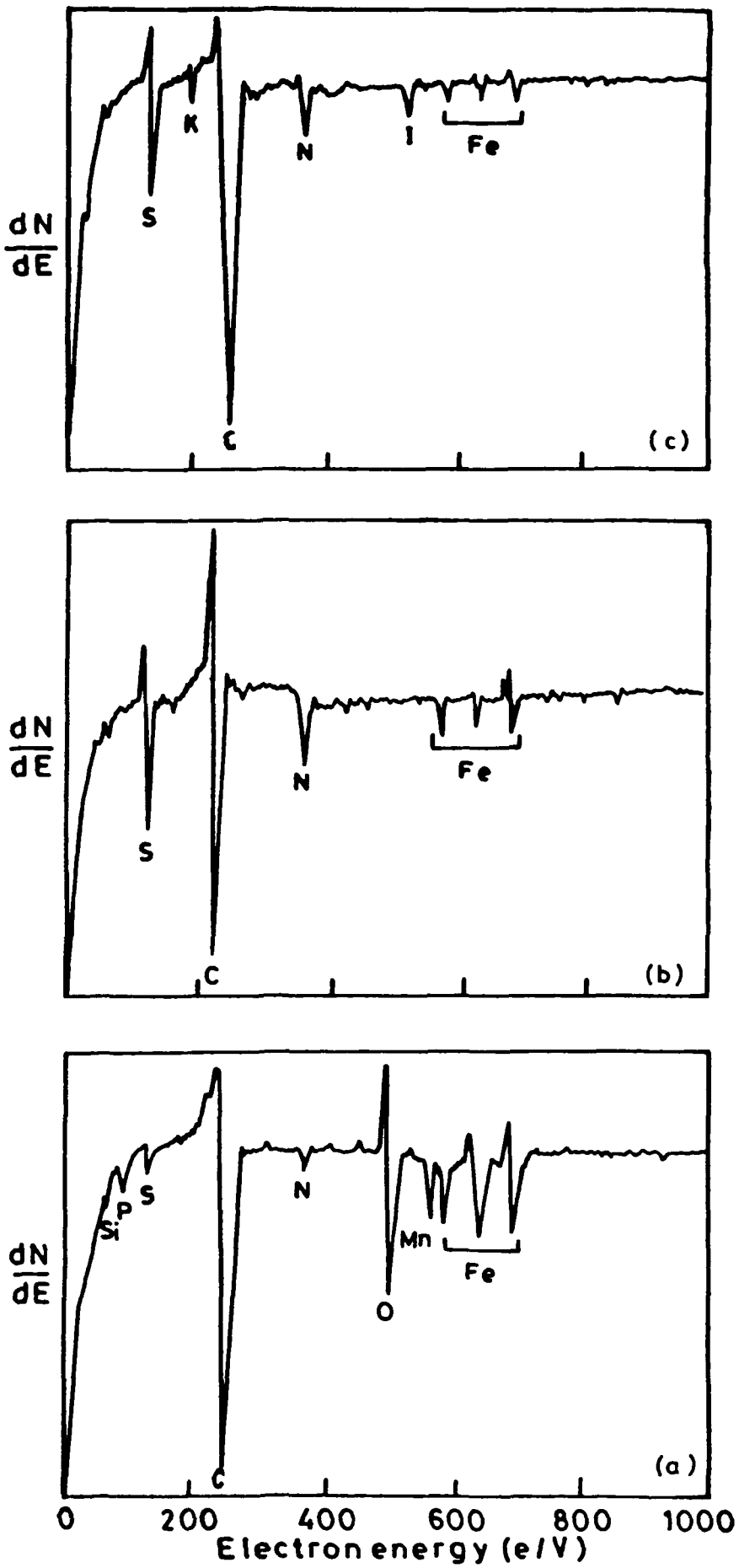


FIGURE 3.1.11 Auger electron spectrum for :–

(a) polished mild steel surface (b) mild steel exposed to PTAT

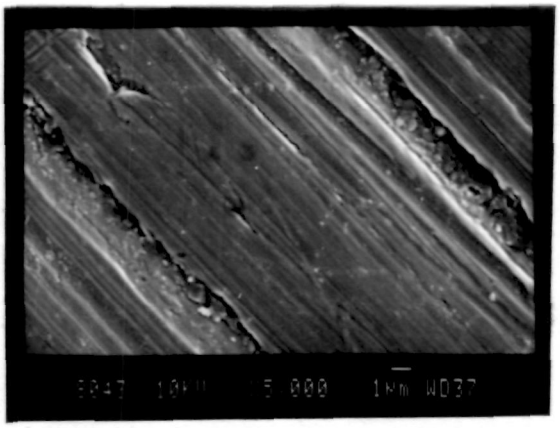
(c) mild steel exposed to PTAT+ KI

Table 3.1.14 - Elemental composition of mild steel obtained from auger electron spectroscopy in presence of PTAT and PTAT + KI in 1N HCl.

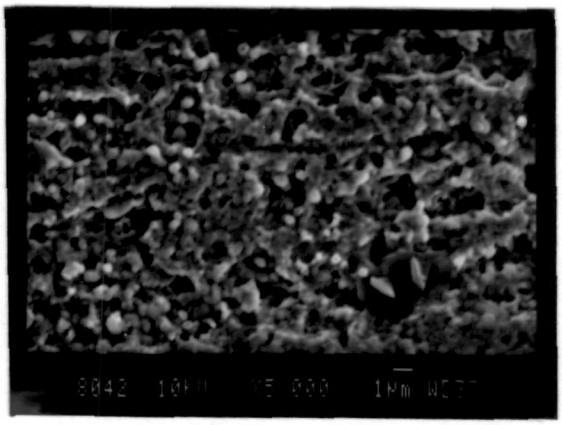
Element	Peak height (mm)	Relative senstivity (S_x)	Composition (%)
Mild Steel			
C	122	0.20	57.50
O	73	0.50	13.80
P	10	0.50	1.81
S	9	0.80	1.06
N	4	0.32	1.18
Mn	22	0.23	9.02
Si	2	0.35	0.54
Fe	32	0.20	15.09
PTAT			
C	130	0.20	73.86
S	52	0.80	7.39
N	24	0.32	8.52
Fe	18	0.20	10.23
PTAT + KI			
C	126	0.20	74.50
S	49	0.80	7.24
N	18	0.32	6.65
Fe	12	0.20	7.10
K	8	0.80	1.18
I	9	0.32	3.33

3.1.6 SCANNING ELECTRON MICROSCOPIC STUDIES

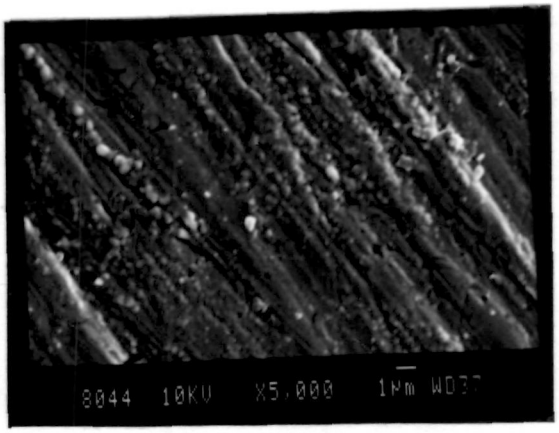
The SEM photographs [Figure 3.1.12 (a - c)] clearly reveal that surface of mild steel and mild steel exposed to 1N HCl containing PTAT are smooth as compared to mild steel exposed to 1N HCl which has shown corroded rough surface. These observations indicate that PTAT inhibits the mild steel corrosion by forming a adsorbed film on the mild steel.



(a)



(b)



(c)

FIGURE 3.1.12 Scanning electron micrographs for :–
(a) Polished mild steel (b) Mild steel in 1N HCl
(c) Mild steel in 1N HCl + 500 ppm PTAT

3.1.7 CONCLUSIONS

The main conclusions drawn from these studies are :–

1. *All the investigated macrocyclic compounds show good inhibition efficiency* in the acid solutions.
2. The I E of all macrocyclic compounds increases with the increase in inhibitor concentration and immersion period, whereas decreases with the increase of temperature and acid concentration.
3. The I E of all the macrocyclic compounds follows the order :–

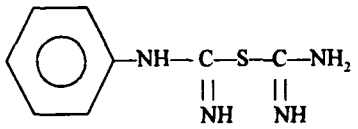
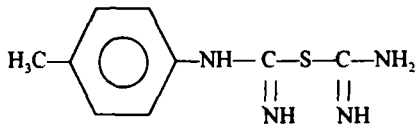
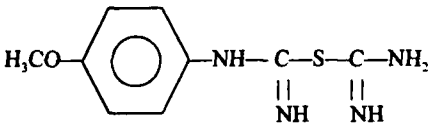
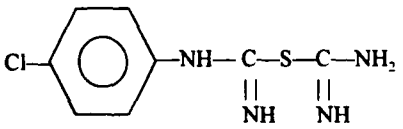
   PTAT > PTAB > POAB; TBOAD > DBOAD > BMOAT > BOAH > MOAT > OAH
4. The I E of all the tested compounds increased on addition of KI due to synergistic effect .
5. The adsorption of all the compounds on the mild steel surface from the all acidic solutions obeys Temkin's adsorption isotherm.
6. PTAT, PTAB, POAB, TBOAD and DBOAD behave mixed inhibitors whereas BMOAT, MOAT, BOAH and OAH behave as mixed inhibitors in HCl and predominantly cathodic in H_2SO_4 .
7. PTAT, PTAB and POAB increase R_t values and decrease I_{corr} and C_{dl} values in 1N HCl.
8. PTAT, PTAB and POAB reduce hydrogen permeation current considerably in 1N HCl.
9. AES studies *confirm the adsorption of macrocyclic compound through* nitrogen and sulphur atoms.
10. SEM photographs of mild steel exposed to 1N HCl and PTAT show smooth surface as compared to mild steel exposed to 1N HCl.

SECTION 2

THIOAMIDINES : A NEW CLASS OF ACID CORROSION INHIBITORS

The organic compounds containing both nitrogen and sulphur atoms are widely used as corrosion inhibitors because they give the better inhibition efficiency than those containing N or S atoms alone [27 - 28]. Among these thiourea and its derivatives have been investigated extensively [29 - 33], but Schmitt [34] has reported that thiourea derivatives are highly toxic and induce permeation of hydrogen into the metal causing embrittlement, therefore their use as corrosion inhibitor is not safe. To obviate all of these drawbacks we have synthesized four substituted Thiobisformamidines starting from different p-substituted thiourea to study the corrosion inhibiting behavior of mild steel in acid medium. The selection of these compounds is based on the fact that they get adsorbed readily on the metal surface through nitrogen and sulphur atoms, the toxicity of these compounds is very low [35] and they are readily soluble in acid solution. The molecular structure of these compounds are shown in Table 3.2.1.

TABLE 3.2.1 NAME AND STRUCTURAL FORMULAE OF THE INHIBITORS USED

S.No.	STRUCTURAL FORMULA	DESIGNATION AND ABBRIVIATION
1		Phenyl Thiobisformamidine (PTBF)
2		Tolyl Thiobisformamidine (TTBF)
3		Anisidyl Thiobisformamidine (ATBF)
4		4-cholrophenyl Thiobisformamidine (CPTBF)

3.2.1 WEIGHT LOSS STUDIES

The weight loss experiments were conducted in 1 - 5 N HCl on mild steel using different concentrations of four thiobisformamidine compounds. Various parameters obtained from this study such as inhibition efficiency (I E) and corrosion rates (C R) are given in Table 3.2.2.

The results show that increase in inhibitor concentration increased the inhibition efficiency of all the compounds in all of the three acids but after the optimum concentration of each inhibitor no appreciable change in I E was found. The optimum concentration of all the compounds was 500, 700 and 1000 ppm in 1N, 3N and 5N HCl solution respectively. The effect of inhibitor concentration on I E in 1N HCl is shown in Figure 3.2.1 (a).

The values of I E were found to depend on the molecular structure of the investigated compounds. The inhibition efficiencies of these compounds has been found to be in the following order :—

CPTBF > ATBF > TTBF > PTBF

Among these compounds the chloro derivative showed the highest I E which may be attributed to the fact that its dipole moment is more than that of the other compounds. Smialowaska et al. [36] and Gad - Allah co - workers [37] have also found that chlorothiophene and chloroaminopyrazole show higher I E than their corresponding parent compounds.

The better performance of methoxy derivative (ATBF) than methyl substituted thiobisformamidine (TTBF) can be explained on the basis of " Pearson's hard and soft acid base principle" (HSAB) [38, 39]. Methoxy derivative being a hard base forms a strong bond with ferrous and ferric ions which leads to more adsorption and inhibition .In case of methyl substituted thiobisformamidines the inductive effect of methyl group makes the nitrogen center a soft base so ferrous and ferric ions form a weak bond with soft base. This may lead to lesser adsorption and inhibition than methoxy derivative.

The I E of thiobisformamidines was found to decrease with the increase in

Table 3.2.2 - Corrosion parameters obtained from weight loss measurements for mild steel in 1N, 3N and 5N HCl containing different concentrations of substituted thiobisformamidines compounds at 40°C for 3 hours.

Inhi. conc. (ppm)	CPTBF		ATBF		TTBF		PTBF	
	I E (%)	C R (mmpy)	I E (%)	C R (mmpy)	I E (%)	C R (mmpy)	I E (%)	C R (mmpy)
1 N HCl	--	16.80	--	16.80	--	16.80	--	16.80
25	80.1	3.34	74.3	4.31	72.1	4.69	71.2	4.82
50	85.1	2.50	79.1	3.52	77.9	3.71	77.1	3.85
100	88.9	1.85	86.1	2.32	84.2	2.64	82.6	2.92
200	94.2	0.97	91.4	1.43	90.1	1.67	87.1	2.18
300	96.1	0.65	94.4	0.92	93.6	1.30	91.7	1.39
400	98.1	0.32	97.2	0.46	96.1	0.65	92.5	1.25
500	99.4	0.09	99.1	0.13	98.1	0.32	95.1	0.83
3 N HCl	--	57.70	--	57.70	--	57.70	--	57.70
100	81.5	10.60	79.1	12.00	76.3	13.60	72.1	16.00
200	86.8	7.61	86.1	7.98	83.1	9.75	79.6	11.70
300	91.6	4.82	90.1	5.71	88.1	6.82	84.4	8.96
400	94.1	3.38	92.5	4.31	91.7	4.78	86.1	7.98
500	96.9	1.76	94.1	3.43	92.6	4.27	88.2	6.77
600	97.9	1.20	93.4	2.04	95.9	2.36	91.1	5.15
700	99.3	0.37	98.2	1.02	97.1	1.67	92.1	4.50
5 N HCl	--	139.40	--	139.40	--	139.40	--	139.40
200	74.1	36.10	72.1	38.90	65.1	48.80	54.7	63.00
300	79.9	28.00	78.7	29.20	71.5	39.60	63.1	51.50
500	89.1	15.30	86.4	18.90	82.1	25.00	78.5	29.90
700	94.1	8.26	91.2	12.20	89.1	15.10	81.1	19.30
1000	98.1	2.64	97.1	9.04	95.4	8.26	94.1	8.26

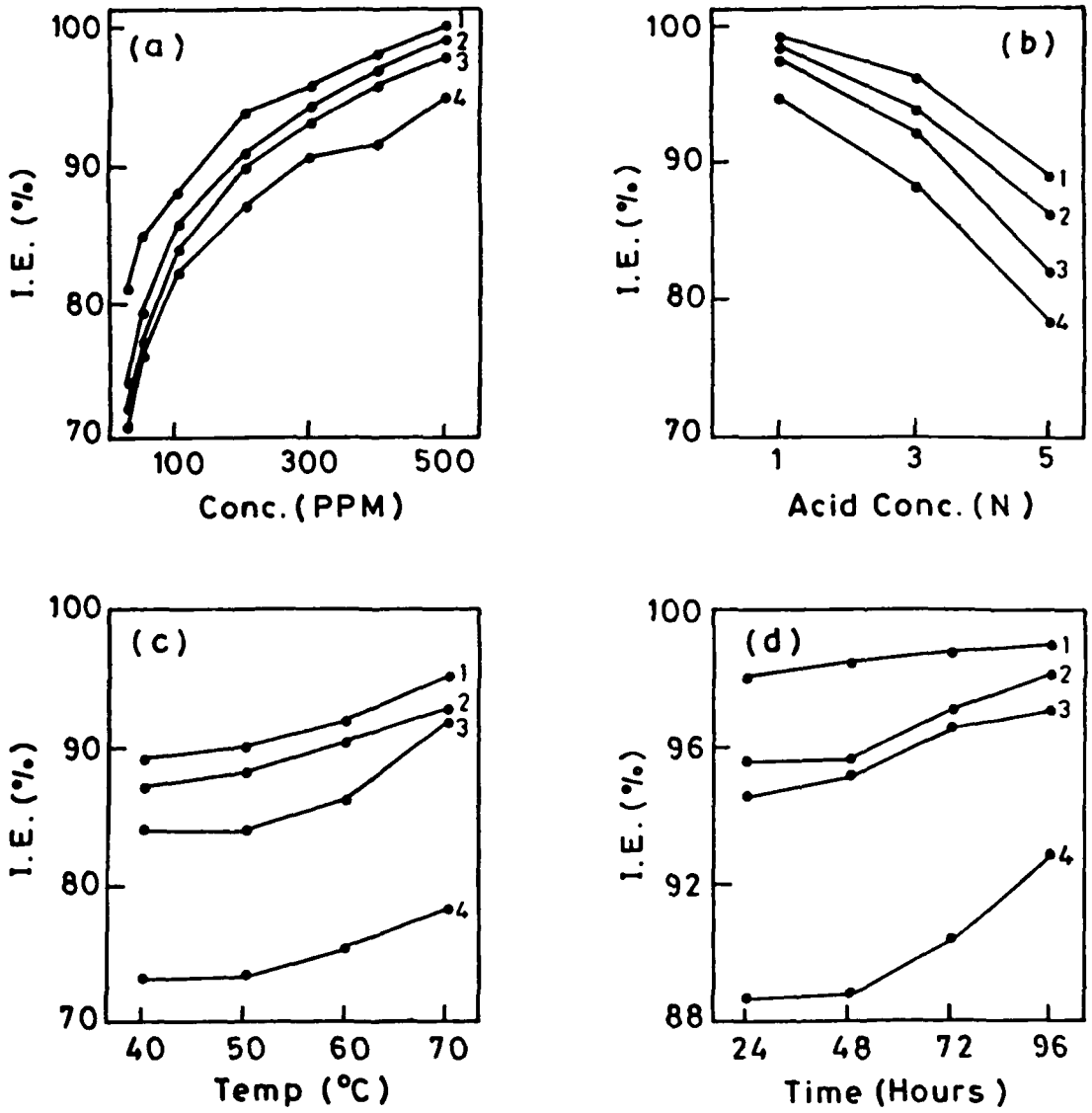


FIGURE 3.2.1 Variation of inhibition efficiency with :-

(a) Inhibitor concentration (ppm) at 40°C in 1N HCl

(b) Concentration (N) of HCl cotaining 500 PPM of inhibitor at 40°C

(c) Temp. (°C) in 1 N HCl cotaining 500 PPM of inhibitor

(d) Immersion time (hours) at room temp. 35 ± 2°C in 1 N HCl containing 500 ppm concentration of inhibitors

1. CPTBF 2. ATBF 3. TTBF 4. PTBF

acid concentration from 1N to 5N HCl Figure 3.2.1 (b). This shows that at high acid concentration inhibitor gets desorbed from the metal surface as compared to low concentrations of acid.

The effect of temperature ranging from 40 - 70°C for an optimum concentrations of each inhibitor in 1N HCl has been shown in the Figure 3.2.1 (c). The results show that the inhibition efficiency increases with the increase in temperature.

The variation of I E with immersion time in 1N HCl has been shown in Figure 3.2.1 (d). It has been observed that I E increases with the increase in immersion time, this indicates that the protective film formed on the metal surface in presence of thiobisformamidine becomes almost nonporous after 48 hours, which does not allow the frequent attack of acid and thus decreases hydrogen evolution.

The values of I E for specific concentrations of inhibitor in combination with KI are given in Table 3.2.3 and show that I E increases on addition of iodide ions for all of the compounds due to synergism. The protonated thiobisformamidines and iodide ions get jointly adsorbed on the metal surface and bring about improved inhibition of the steel surface.

Table 3.2.3- Inhibition efficiencies of substituted thiobisformamidines obtained from weight loss measurements in absence and presence of KI.

Inhi. Conc. (ppm)	KI Conc. (%)	I E (%)			
		CPTBF	ATBF	TTBF	PTBF
1 N HCl					
300	--	96.13	94.48	93.65	91.71
300	0.02	98.34	96.69	95.30	94.75
3 N HCl					
500	--	96.94	94.11	92.60	88.26
500	0.05	98.79	97.59	96.95	93.25
5 N HCl					
700	--	94.17	91.21	89.11	81.12
700	0.10	96.80	95.34	93.87	93.28

The values of inhibition efficiencies and corrosion rates obtained in presence of different concentrations of thiobisformamidines compounds in 5N HCl at 70° C for 30 minutes are given in Table 3.2.4. All the tested compounds have shown maximum inhibition efficiency at 3000 ppm. The I E of all the tested compounds increased by nearly 10 % on addition of small amount (0.25 %) of KI to inhibited solution [Table 3.2.4].

Table 3.2.4- Corrosion parameters obtained from weight loss studies for mild steel in 5N HCl containing different concentrations of substituted thiobisformamidines with and without KI (0.25 %) at 70°C for 30 minutes.

Inhi. Conc. (PPM)	CPTBF		ATBF		TTBF		PTBF	
	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)
5 N HCl	–	1366.2	–	1366.2	–	1366.2	–	1366.2
500	40.8	901.7	37.6	950.1	31.6	1041.2	31.3	1045.6
1000	50.8	749.7	49.2	773.7	44.5	845.6	42.7	872.9
1500	57.1	653.8	52.2	728.3	52.7	720.6	52.2	728.3
2000	68.1	484.7	58.1	638.6	57.6	645.3	60.8	597.2
3000	70.2	454.2	70.1	455.4	67.7	492.4	60.2	606.3
1000+KI	57.8	642.6	56.1	669.9	55.8	673.8	53.7	704.5
2000+KI	73.1	409.7	71.6	431.9	70.4	451.3	64.8	535.6

3.2.1.1 ADSORPTION ISOTHERM

The adsorption of inhibitor molecule on the steel surface was characterized by plotting the adsorption isotherm. The values of surface coverage (θ) were evaluated in 1 - 5N HCl and Temkin's isotherms were tested by plotting the θ vs log C for all the compounds. A straight line was obtained in all the cases thereby proving the fact that the adsorption of these compounds on the surface of mild steel obeys Temkin's adsorption isotherm [Figure 3.2.2 (a - c)].

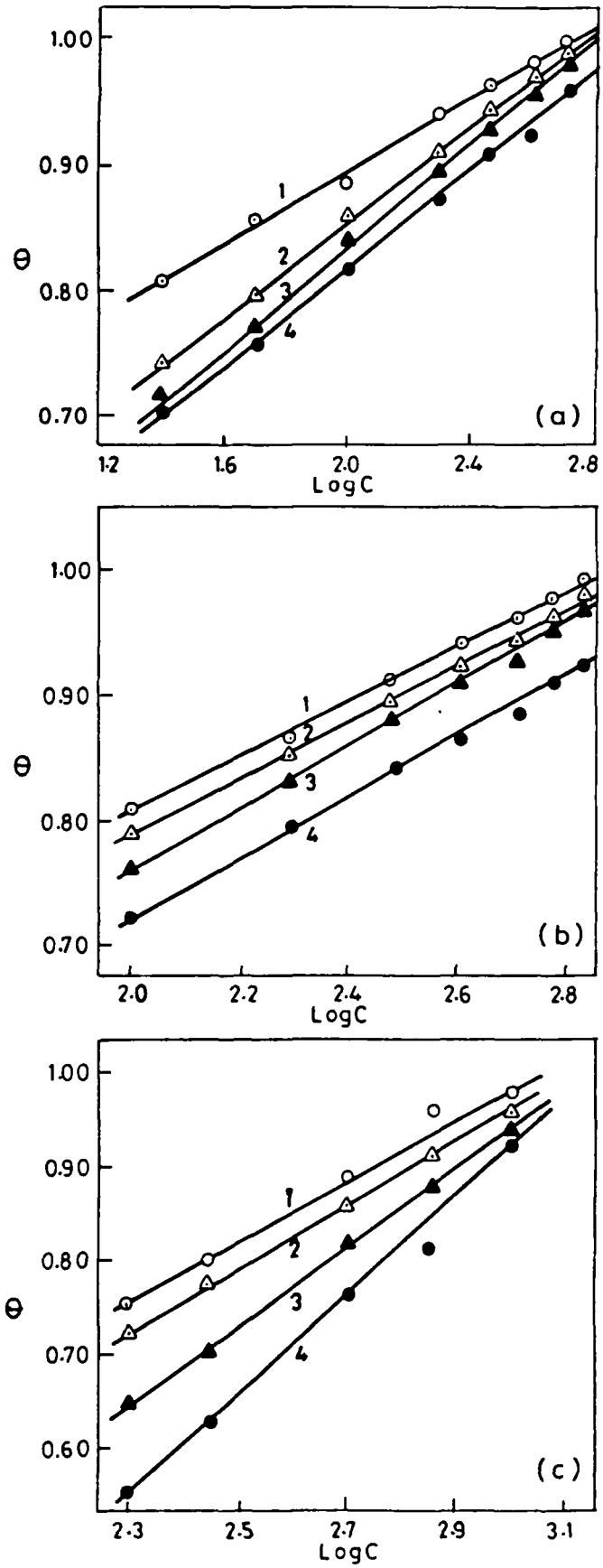


FIGURE 3.2.2 Temkin's adsorption isotherm plots for mild steel in (a) 1 N (b) 3 N (c) 5N HCl containing different concentrations of substituted thiobisformamidines :–
1. CPTBF 2. ATBF 3. TTBF 4. PTBF

3.2.2 POTENTIODYNAMIC POLARIZATION STUDIES

Both the anodic and cathodic polarization behavior of mild steel in 1 - 5N HCl in absence and presence of these thiobisformamidines are shown in Figure 3.2.3 - 3.2.6. Various electrochemical corrosion parameters calculated from Tafel plots such as corrosion current density (I_{corr}), Corrosion potential (E_{corr}), Tafel slope constants (b_c and b_a) and inhibition efficiency (I E) are given in Table 3.2.5 - 3.2.7. It is evident from the results that I_{corr} values decrease considerably in the presence of different concentrations of inhibitors and maximum decrease in I_{corr} value is obtained at a concentration of 500, 700 and 1000 ppm in 1N, 3N and 5N HCl respectively.

E_{corr} values do not show any significant shift in presence of these compounds. These observations clearly indicate that the inhibition of corrosion in presence of these compounds is under mixed control. The b_c and b_a values do not change very much in presence of inhibitors, this suggests that inhibition of corrosion takes place by blocking the active sites of metal.

3.2.3 ELECTROCHEMICAL IMPEDANCE STUDIES

Nyquist plots obtained from this study in presence and absence of different inhibitor concentration in 1N HCl are shown in Figure 3.2.7. Various parameters such as charge transfer resistance (R_t) , double layer capacitance (C_{dl}), corrosion current density (I_{corr}) and inhibition efficiency (I E) obtained from this study are given in Table 3.2.8. It is seen from the table that the presence of inhibitor increases the R_t values and brings down the values of C_{dl} and I_{corr} .These observations suggest that these compounds inhibit corrosion of mild steel by blocking the double layer. Maximum decrease in C_{dl} and I_{corr} has been observed in cases of CPTBF suggesting that CPTBF is the most effective corrosion inhibitor.

3.2.4 HYDROGEN PERMEATION STUDIES

Hydrogen permeation studies have been carried out for the optimum

Table 3.2.5- Potentiodynamic electrochemical parameters for mild steel in 1N HCl containing different concentrations of substituted thiobisformamidines at 35°C.

Inhi. Conc. (ppm)	I_{corr} (μAcm^{-2})	E_{corr} (mv)	b_c (mv dec^{-1})	b_a (mv dec^{-1})	IE (%)
1N HCl	350	-554	130	60	--
CPTBF					
50	140	-550	120	50	60.00
100	130	-552	130	55	62.86
300	62	-550	140	50	82.29
400	66	-554	130	50	81.14
500	44	-556	125	45	87.43
ATBF					
50	155	-556	120	48	55.71
100	140	-558	130	58	60.00
300	130	-554	120	60	62.86
400	100	-552	130	55	71.43
500	90	-556	130	50	74.29
TTBF					
50	155	-552	130	50	55.71
100	150	-554	130	50	57.14
300	140	-552	128	48	60.00
400	130	-556	130	50	62.86
500	120	-554	120	55	65.71
PTBF					
50	200	-556	120	50	42.86
100	150	-554	120	50	57.14
300	140	-552	130	55	60.00
400	130	-550	125	60	62.86
500	120	-554	130	50	65.71

Table 3.2.6- Potentiodynamic electrochemical parameters for mild steel in 3 N HCl containing different concentrations of substituted thiobisformamidines at 35°C.

Inhi. Conc. (ppm)	I_{corr} (μAcm^{-2})	E_{corr} (mv)	b_c (mv dec^{-1})	b_a (mv dec^{-1})	IE (%)
3N HCl	1200	-568	130	70	--
CPTBF					
100	170	-564	120	45	85.83
300	130	-568	125	50	89.17
500	93	-570	130	60	92.25
700	60	-572	130	50	95.00
ATBF					
100	200	-566	110	48	83.33
300	120	-570	108	40	90.00
500	110	-568	100	40	90.83
700	100	-572	110	50	91.67
TTBF					
100	180	-570	100	50	85.00
300	130	-572	110	50	89.17
500	105	-568	110	45	91.25
700	110	-574	110	45	90.83
PTBF					
100	300	-566	120	50	75.00
300	240	-570	130	55	80.00
500	190	-572	120	50	84.17
700	180	-568	135	60	85.00

Table 3.2.7- Potentiodynamic electrochemical parameters for mild steel in 5N HCl containing different concentrations of substituted thiobisformamidines with and without (0.25%) KI at 35°C.

Inhi. Conc. (ppm)	I_{corr} (μAcm^{-2})	E_{corr} (mv)	b_c (mv dec^{-1})	b_a (mv dec^{-1})	IE (%)
5N HCl	4000	-520	130	80	--
5N HCl+ KI	580	-516	130	58	85.50
CPTBF					
300	500	-524	115	50	87.50
500	350	-526	120	60	91.25
700	230	-522	110	60	94.25
1000	190	-524	110	60	95.25
500+KI	220	-526	120	50	94.50
700+KI	200	-524	130	60	95.00
ATBF					
300	720	-518	120	54	82.00
500	500	-522	130	54	87.50
700	240	-518	125	54	94.00
1000	230	-524	120	50	94.25
500+KI	230	-526	120	70	94.25
700+KI	220	-528	120	60	94.50
TTBF					
300	900	-522	130	60	77.50
500	500	-524	120	60	87.50
700	540	-526	110	50	86.50
1000	370	-528	120	60	90.75
500+KI	380	-522	110	60	90.50
700+KI	360	-524	120	60	91.00
PTBF					
300	800	-524	120	60	80.00
500	580	-522	110	50	85.50
700	560	-528	120	60	86.00
1000	300	-526	120	60	92.50
500+KI	480	-520	120	55	88.00
700+KI	340	-524	120	50	91.50

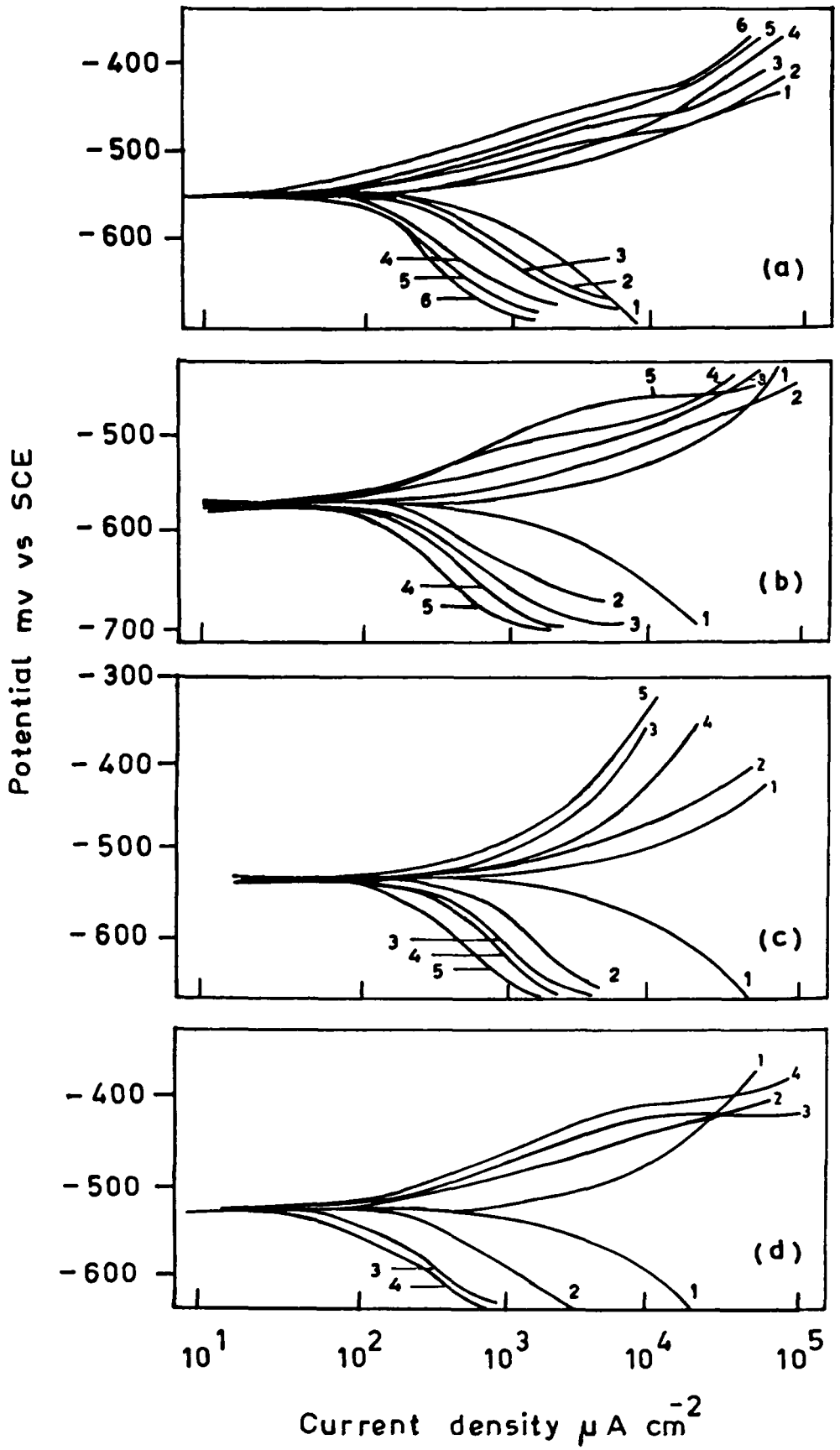


FIGURE 3.2.3 Potentiodynamic polarization curves for mild steel containing different concentrations of CPTBF in : –

(a) 1N HCl : 1. Blank 2. 50 ppm 3. 100 ppm 4. 300 ppm 5. 400 ppm 6. 500 ppm
(b) 3N HCl : 1. Blank 2. 100 ppm 3. 300 ppm 4. 500 ppm 5. 700 ppm
(c) 5N HCl : 1. Blank 2. 300 ppm 3. 500 ppm 4. 700 ppm 5. 1000 ppm
(d) 5N HCl : 1. Blank 2. 5N HCl + KI 3. 500ppm + KI 4. 700 ppm + KI

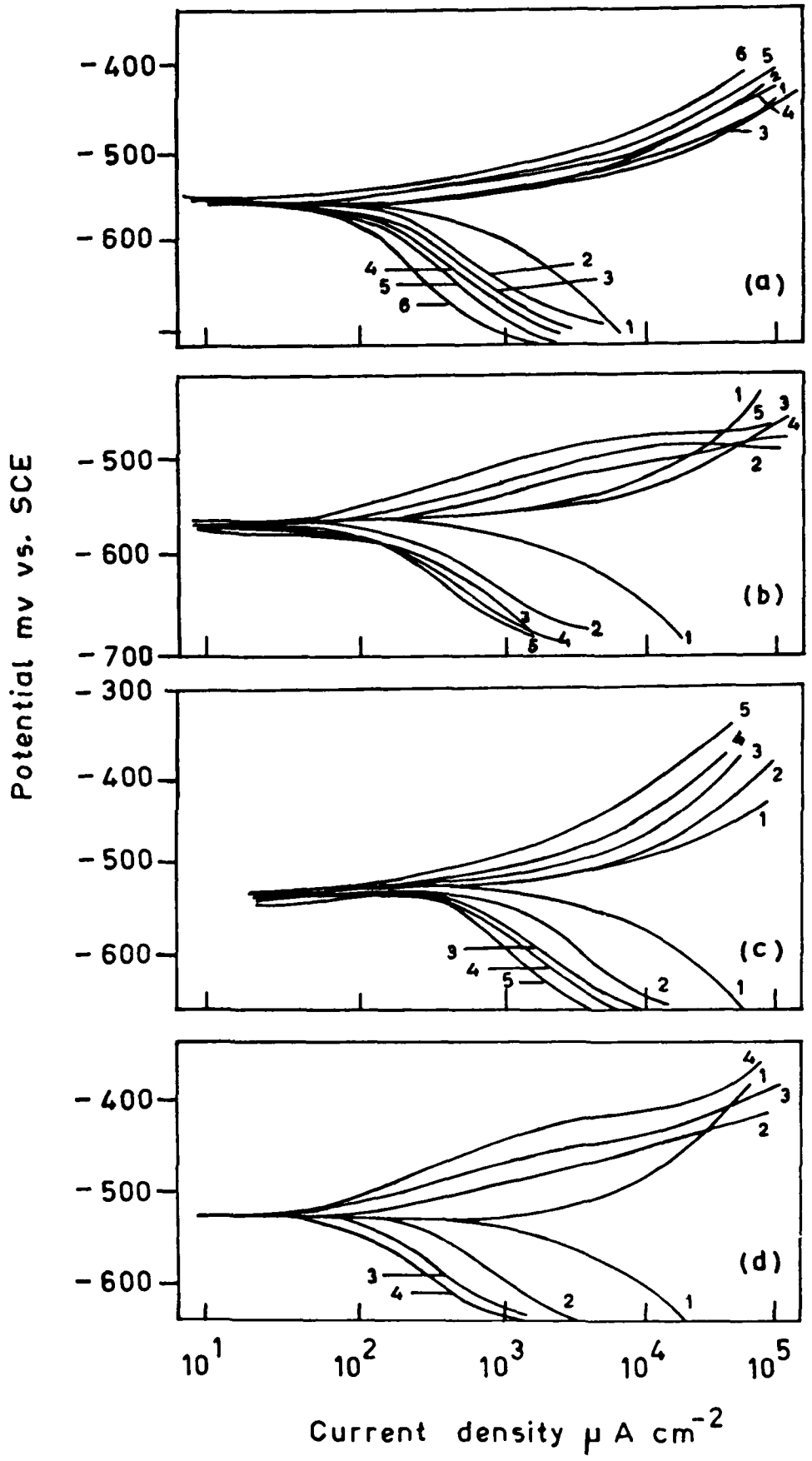


FIGURE 3.2.4 Potentiodynamic polarization curves for mild steel containing different concentrations of ATBF in : –

(a) 1N HCl :	1. Blank	2. 50 ppm	3. 100 ppm	4. 300 ppm	5. 400 ppm	6. 500 ppm
(b) 3N HCl :	1. Blank	2. 100 ppm	3. 300 ppm	4. 500 ppm	5. 700 ppm	
(c) 5N HCl :	1. Blank	2. 300 ppm	3. 500 ppm	4. 700 ppm	5. 1000 ppm	
(d) 5N HCl :	1. Blank	2. 5N HCl + KI	3. 500ppm + KI	4. 700 ppm + KI		

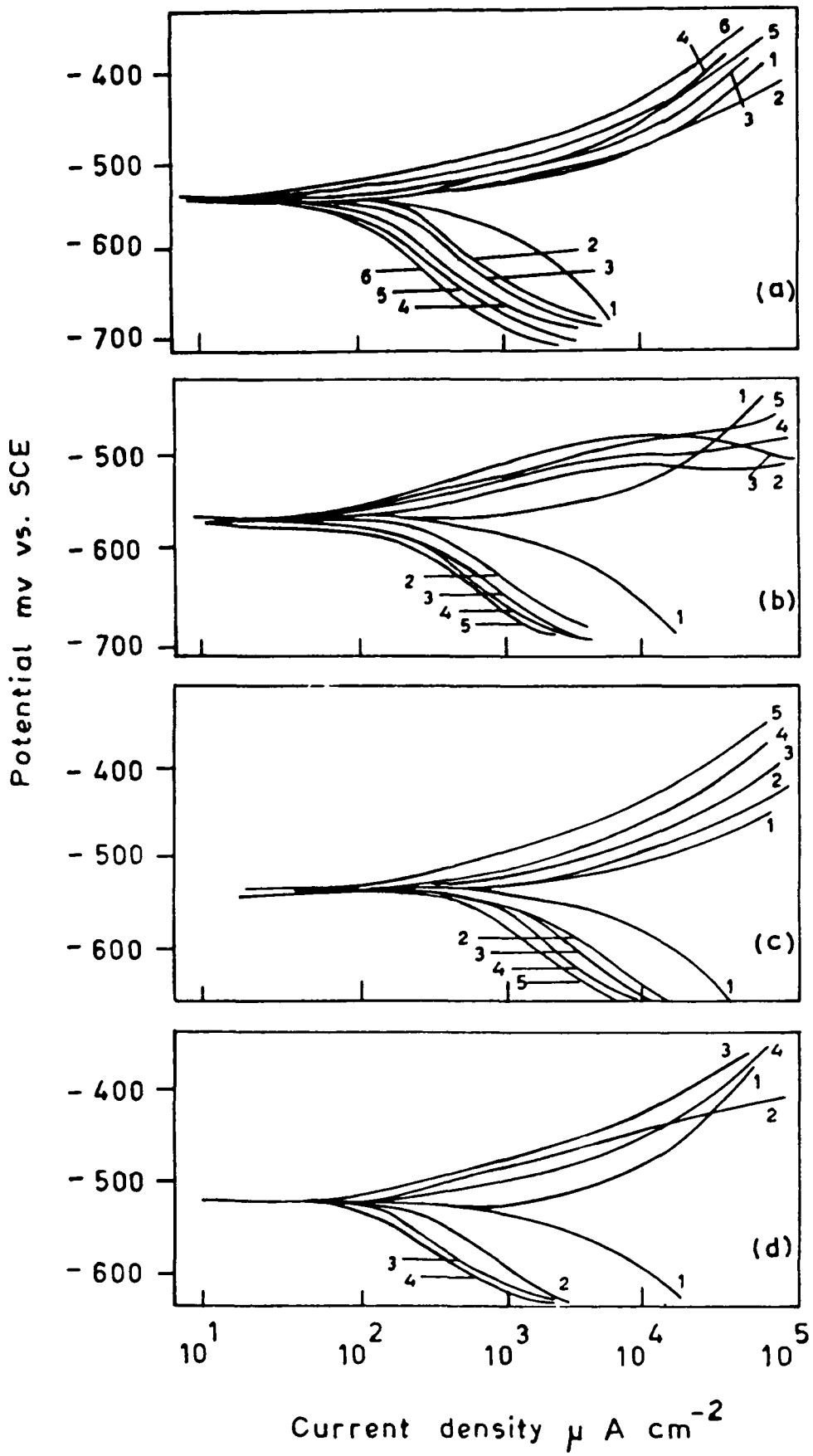


FIGURE 3.2.5 Potentiodynamic polarization curves for mild steel containing different concentrations of TTBF in : –

(a) 1N HCl	1. Blank	2 50 ppm	3 100 ppm	4 300 ppm	5. 400 ppm	6. 500 ppm
(b) 3N HCl	1 Blank	2 100 ppm	3 300 ppm	4. 500 ppm	5 700 ppm
(c) 5N HCl	1 Blank	2 300 ppm	3 500 ppm	4. 700 ppm	5. 1000 ppm
(d) 5N HCl	1 Blank	2 5N HCl + KI	3 500ppm + KI	4 700 ppm + KI

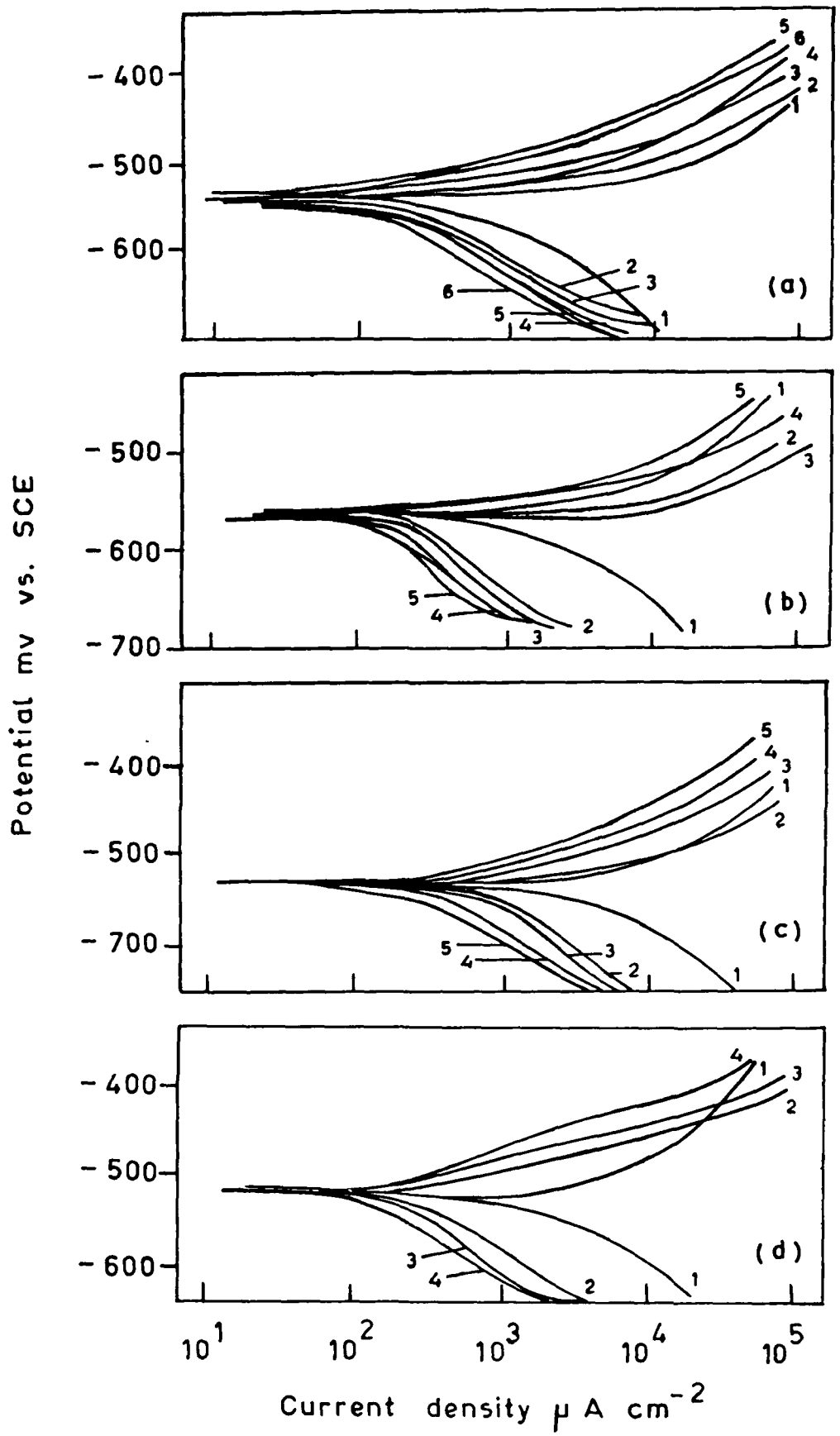


FIGURE 3.2.6 Potentiodynamic polarization curves for mild steel containing different concentrations of PTBF in : –

(a) 1N HCl :	1. Blank	2. 50 ppm	3. 100 ppm	4. 300 ppm	5. 400 ppm	6. 500 ppm
(b) 3N HCl :	1. Blank	2. 100 ppm	3. 300 ppm	4. 500 ppm	5. 700 ppm	
(c) 5N HCl :	1. Blank	2. 300 ppm	3. 500 ppm	4. 700 ppm	5. 1000 ppm	
(d) 5N HCl :	1. Blank	2. 5N HCl + KI	3. 500ppm + KI	4. 700 ppm + KI		

concentration (500 ppm) of CPTBF and PTBF in 1N HCl and results are shown in Figure 3.2.8. It is seen that both the compounds bring down permeation current. The reduction of hydrogen permeation current by CPTBF is higher than that of PTBF. The reduction in hydrogen permeation current is attributed to the adsorption of inhibitors on the metal surface which prevents the entry of hydrogen into the metal.

Table 3.2.8 -Impedance data of mild steel in 1N HCl containing different concentrations of substituted thiobisformamidine compounds.

SYSTEM	Inhi. Conc. (ppm)	R_t (Ω cm^2)	C_{dl} (μF cm^{-2})	I_{corr} (μ A cm^{-2})	I E (%)
1N HCl	--	115	12832	155	--
CPTBF	300	2273	888	7.01	94.94
	500	2660	658	5.41	95.68
ATBF	300	1855	965	8.18	93.80
	500	2400	806	7.00	95.21
TTBF	300	1727	1023	9.72	93.34
	500	2300	762	6.82	95.00
PTBF	300	1309	1259	13.28	91.21
	500	1600	1072	9.81	92.81

Table 3.2.9 - Hydrogen permeation parameters for mild steel in 1N HCl containing 500 ppm of substituted thiobisformamidines at 35 ± 2°C.

Inhi. Conc. (ppm)	Permeation current (μ A)	Percent reduction (%)
1N HCl	24	--
500 CPTBF	13	45.8
500 PTBF	13.8	42.5

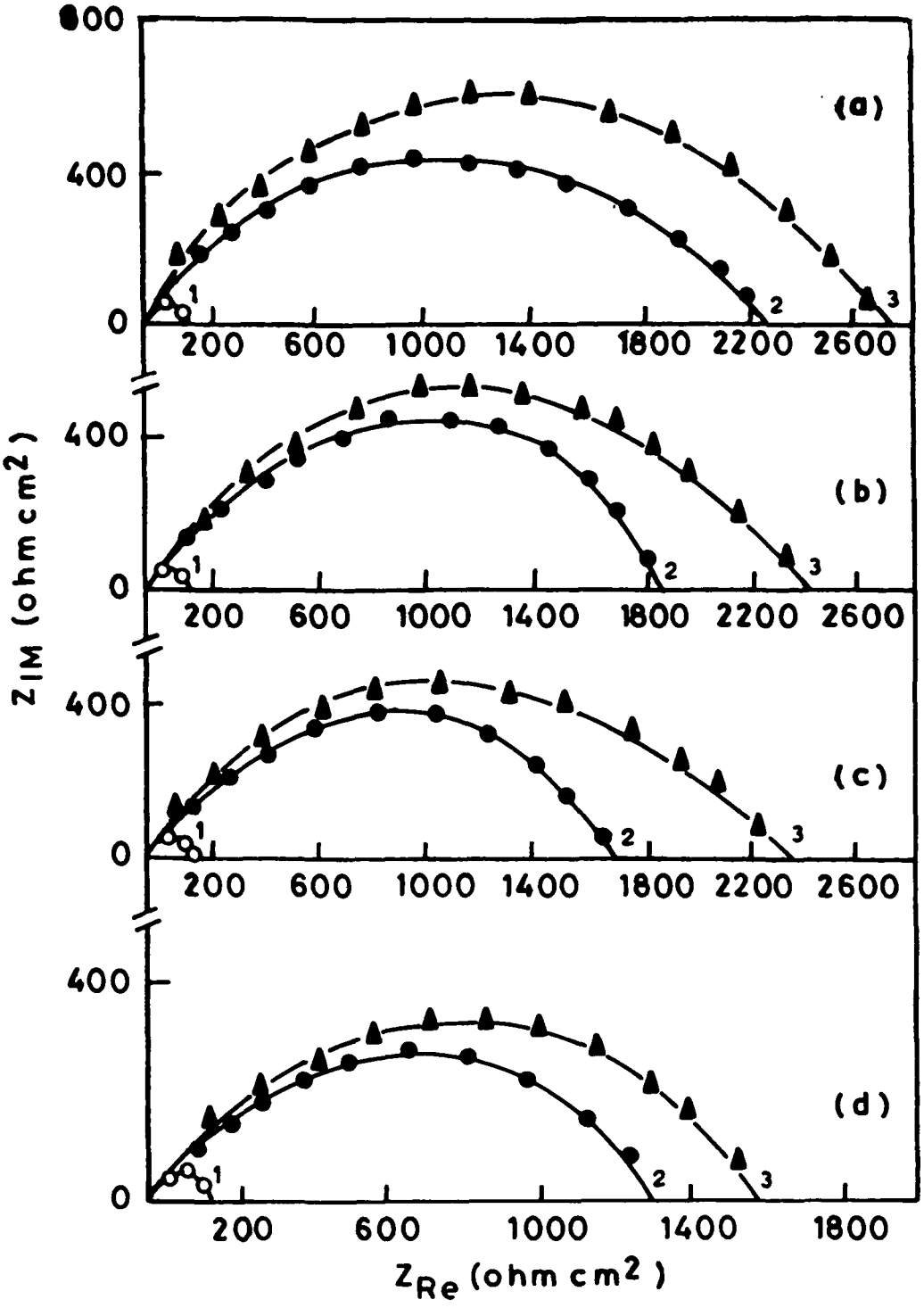


FIGURE 3.2.7 Nyquist plots for mild steel in 1N HCl in absence and presence of different concentrations of substituted thiobisformamidines :–
(a) CPTBF (b) ATBF (c) TTBF (d) PTBF 1. Blank 2. 300 ppm 3. 500 ppm

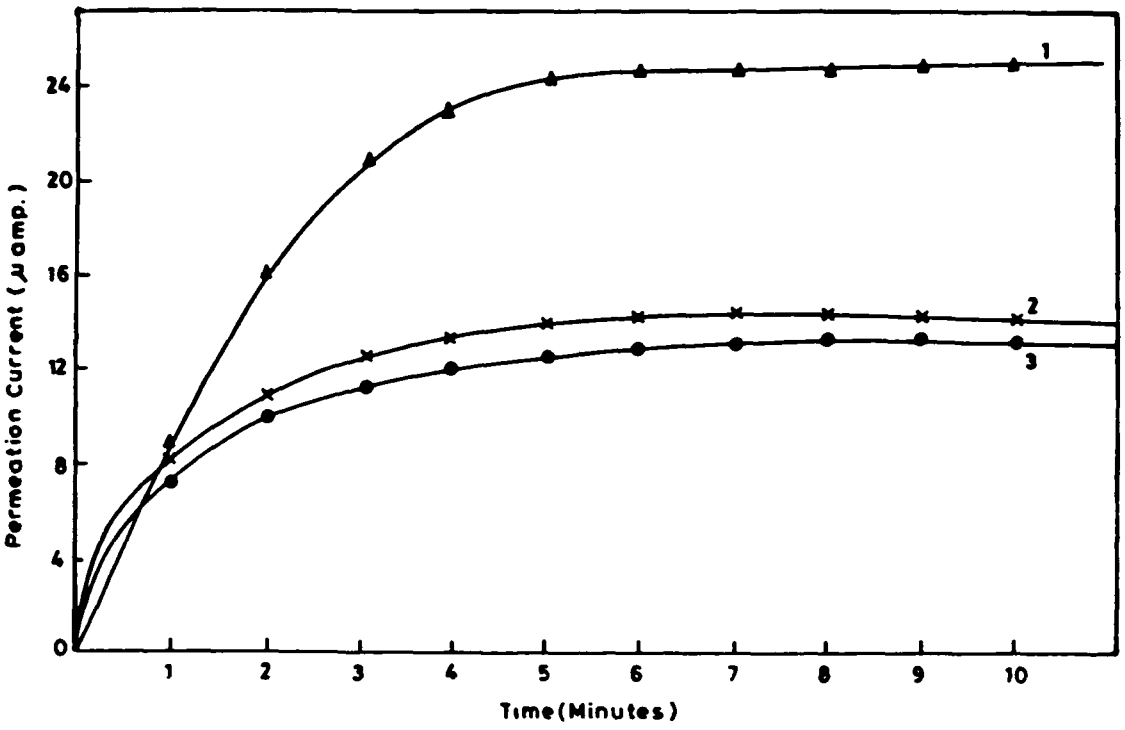


FIGURE 3.2.8 Hydrogen permeation curves for mild steel in 1N HCl in absence and presence of 500 PPM of substituted thiobisformamidines

1 Blank 2 PTBF 3 CPTBF

3.2.5 AUGER ELECTRON SPECTROSCOPY

Auger electron spectrum for mild steel exposed to 1N HCl containing 500 ppm of CPTBF and CPTBF + KI are shown in Figure 3.2.9 (a - c). The peaks at 148, 187 and 388 ev respectively indicate the adsorption of this compound on the metal surface through the sulphur, chlorine and nitrogen atoms respectively.

AES spectrum for mild steel obtained with 300 ppm CPTBF and 0.02 % KI exhibits peaks at 152, 186, 389 and 511 ev respectively for sulphur, chlorine, nitrogen and iodine. These observations clearly prove the adsorption of CPTBF along with K I.

The values of atomic concentration of different elements present on the mild steel surface in the adsorbed inhibitor film are given in Table 3.2.10. These values indicate the concentration of nitrogen, sulphur, chlorine and iodine present in adsorbed inhibitor film.

3.2.6 SCANNING ELECTRON MICROSCOPIC STUDIES

SEM micrographs of plain mild steel, steel exposed to 1N HCl and to a solution of 500 ppm CPTBF in 1N HCl are shown in Figure 3.2.10 (a - c). These photographs clearly show the smooth surface of mild steel and steel exposed to CPTBF whereas the rough corroded surface is seen in case of steel exposed to 1N HCl. These observations suggest that CPTBF protects the mild steel surface.

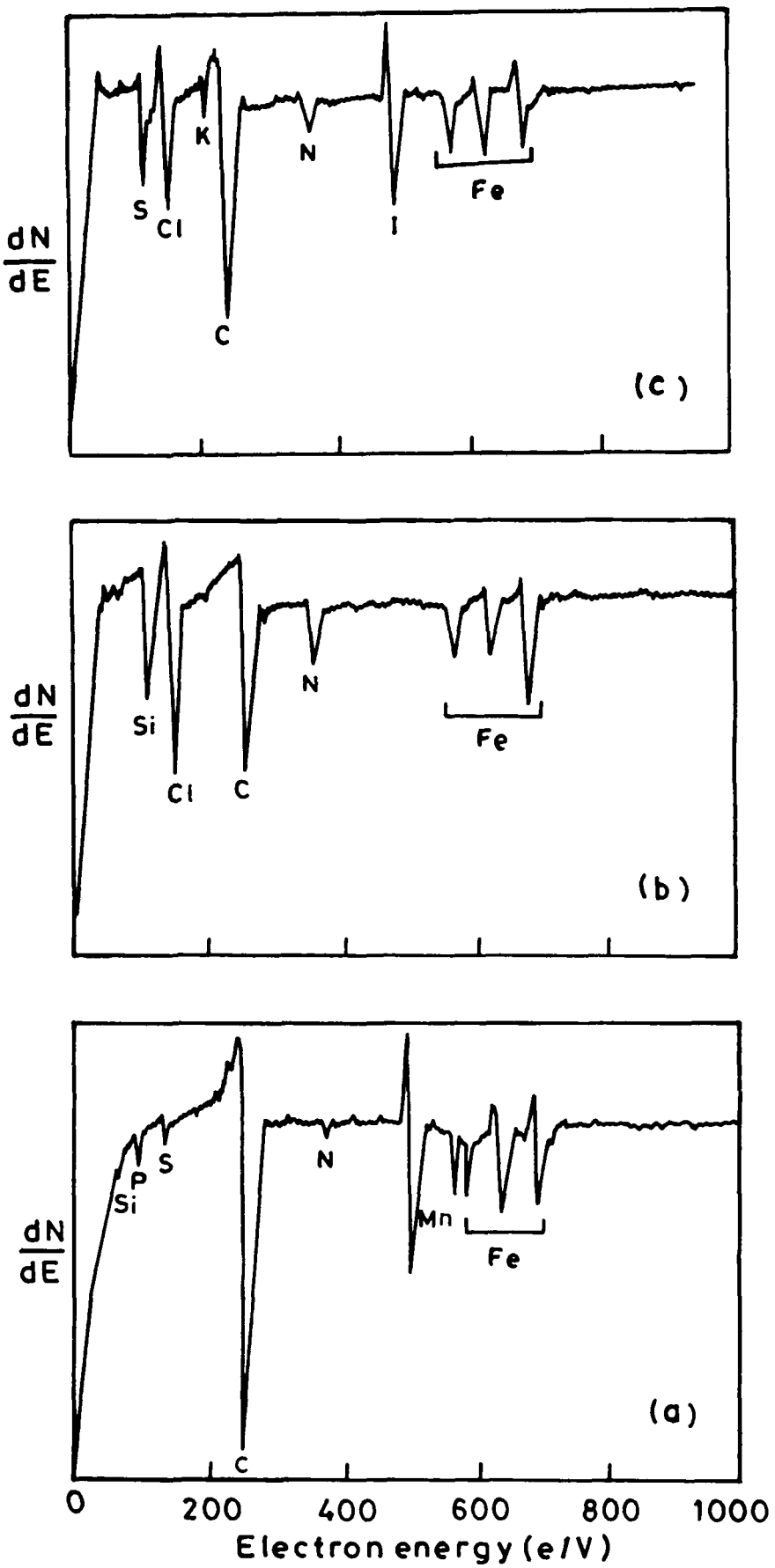
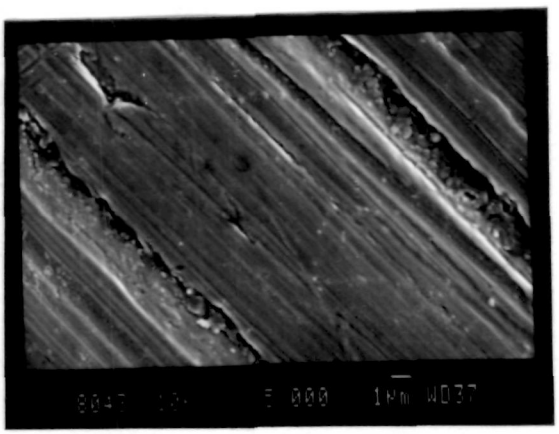


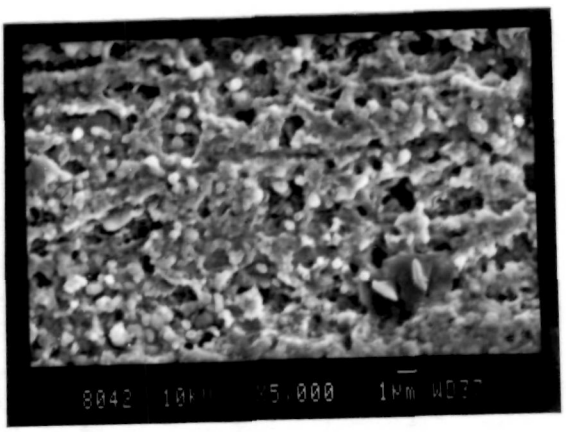
FIGURE 3.2.9 Auger electron spectrum for –
(a) polished mild steel surface (b) mild steel exposed to CPTBF
(c) mild steel exposed to CPTBF +KI

Table 3.2.10 - Elemental composition of mild steel obtained from auger electron spectroscopy in presence of CPTBF and CPTBF + KI in 1N HCl.

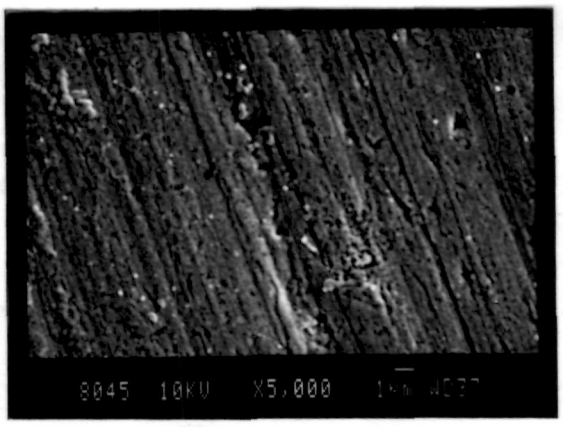
Element	Peak height (mm)	Relative senstivity(S_x)	Composition (%)
Mild steel			
C	122	0.20	57.50
O	73	0.50	13.80
P	10	0.50	1.81
S	9	0.80	1.06
N	4	0.32	1.18
Mn	22	0.23	9.02
Si	2	0.35	0.54
Fe	32	0.20	15.09
CPTBF			
C	65	0.20	46.63
S	32	0.80	5.74
N	24	0.32	10.76
Fe	38	0.20	27.26
Cl	67	1.00	9.16
CPTBF+KI			
C	77	0.20	48.08
S	26	0.80	4.06
N	12	0.32	4.68
Fe	22	0.20	13.74
Cl	52	1.00	6.49
K	12	0.80	1.87
I	54	0.32	21.07



(a)



(b)



(c)

FIGURE 3.2.10 Scanning electron micrographs for :–
(a) Polished mild steel (b) Mild steel in 1N HCl
(c) Mild steel in 1N HCl + 500 ppm CPTBF

3.2.7 CONCLUSIONS

The main conclusions drawn from these studies are:—

1. All the investigated thiobisformamidines have shown good inhibition efficiency in acid solutions (1 - 5 N HCl)
2. The inhibition efficiencies of these thiobisformamidines follow the order :–

   CPTBF > ATBF > TTBF > PTBF
3. The inhibition efficiency of all these investigated thiobisformamidines increases with the increase in inhibitor concentration, temperature and immersion time whereas decreases with the increase in acid concentration.
4. Inhibition efficiency of all the tested compounds increases on the addition of small amount of KI due to synergism.
5. The adsorption of these compounds on the mild steel surface from the acidic solution obeys Temkin's adsorption isotherm.
6. Potentiodynamic polarization study clearly reveals that all the compounds behave as mixed inhibitors in 1 - 5 N HCl solution.
7. Electron impedance studies reveals that the presence of thiobisformamidines results in increase of R_t value and decrease in C_{dl} and I_{corr} values.
8. Hydrogen permeation current decreases in presence of CPTBF and PTBF
9. AES studies reveals that CPTBF adsorbs on the metal surface through N, S and Cl atoms.
10. SEM studies has shown smooth surface of mild steel inhibited with CPTBF.

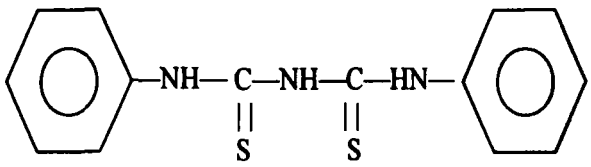
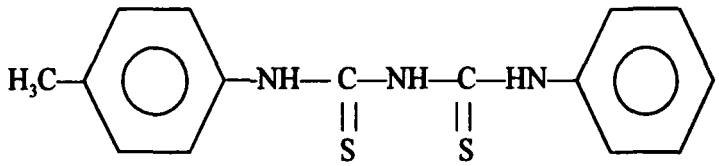
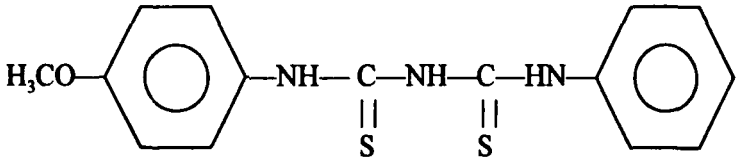
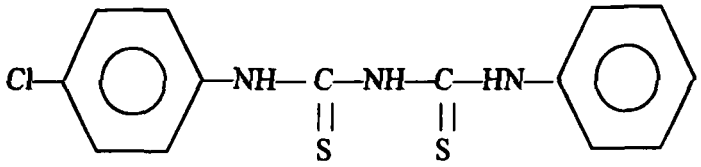
SECTION 3

DITHIOBIURETS : A NOVEL CLASS OF ACID CORROSION INHIBITORS

The inhibitive power of organic corrosion inhibitors has been interpreted in terms of many different characteristics such as molecular size, molecular weight, molecular structure and nature of the heteroatoms present in molecule etc. [40]. The corrosion inhibition characteristics of nitrogen containing organic inhibitors has also been explained [41 - 45]. It is reported that sulphur containing compounds are more effective corrosion inhibitors than nitrogen containing compounds because of the high density of electrons around the sulphur atoms. The compound containing both nitrogen and sulphur atoms has given better inhibition efficiency than those containing N or S atoms alone [46].

To meet the above requirement effectively we have synthesized four substituted dithiobiurets to investigate their inhibiting action on the corrosion of mild steel in 1 - 5N HCl. The structural details of these compounds are given in Table 3.3.1.

TABLE 3.3.1 NAME AND STRUCTURAL FORMULAE OF THE INHIBITORS USED

S.No.	STRUCTURAL FORMULA	DESIGNATION AND ABBRIVIATION
1		1,5-diphenyl-2,4-dithiobiuret (DPDTB)
2		1-tolyl-5-phenyl- 2,4 -dithiobiuret (TPDTB)
3		1-anisidyl-5-phenyl-2,4-dithiobiuret (APDTB)
4		1-chlorophenyl-5-phenyl-2,4 dithiobiuret (CPDTB)

The corrosion inhibition characteristics of these compounds are explained in terms of various factors such as inhibitor concentration, acid concentration, temperature, immersion time and molecular structures. Potentiodynamic polarization and AC impedance techniques were used to investigate the mechanism of the inhibition. SEM and AES studies were used to study the surface topography and composition of the inhibitor film present on the surface of the mild steel.

3.3.1 WEIGHT LOSS STUDIES

Various corrosion parameters such as percentage inhibition efficiency (I E) and corrosion rate (CR) obtained by weight loss method at different inhibitor concentration in 1 - 5N HCl are given in Table 3.3.2. It is evident from these results that all of these compounds inhibit corrosion of mild steel at all concentration under study. The percentage inhibiton efficiency for all the inhibitors increases with the increase in concentration of inhibitors [Figure 3.3.1 (a)]. All of these compounds show their maximum inhibition efficiency at 500, 700 and 1000 ppm in 1N, 3N and 5N HCl respectively. The percentage inhibition efficiency for different dithiobiurets decreased in the following order : –

APDTB > TPDTB> DPDTB > CPDTB

The better performance of APDTB as corrosion inhibitor than TPDTB is attributed to the presence of electron releasing group – OCH_3. Since – OCH_3 is better electron releasing group as compared to – CH_3 group, hence it facilitates greater adsorption of methoxy substituted dithiobiuret (APDTB) on the mild steel surface than methyl substituted (TPDTB). This leads to higher inhibition efficiency of APDTB than TPDTB.

The lowest value of I E for CPDTB among the studied compounds can be explained on the basis of – I effect (Electron withdrawing inductive effect) of chloro group which decreases the electron availability on the reaction site and causes less adsorption of the chloro derivative CPDTB on the metal surface as compared to DPDTB which shows lesser inhibition.

Table 3.3.2 - Corrosion parameters obtained from weight loss measurements for mild steel in 1N, 3N and 5N HCl containing different concentrations of substituted dithiobiurets at 40°C for 3 hours.

Inhi. Conc. (PPM)	APDTB		TPDTB		DPDTB		CPDTB	
	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)
1N HCl	–	16.8	–	16.8	–	16.8	–	16.8
25	96.1	0.65	93.4	1.11	92.3	1.31	88.7	1.91
50	96.4	0.61	93.9	1.02	93.4	1.11	91.2	1.49
100	97.5	0.42	95.6	0.74	94.8	0.88	91.4	1.44
200	98.1	0.33	96.9	0.51	96.1	0.65	93.7	1.07
300	98.3	0.28	97.8	0.37	97.2	0.46	94.5	0.93
400	98.6	0.23	98.1	0.33	97.6	0.42	95.6	0.74
500	98.9	0.19	98.6	0.23	98.1	0.33	95.9	0.71
3N HCl	–	57.8	–	57.8	–	57.8	–	57.8
100	93.6	3.72	93.4	3.67	91.7	4.78	93.1	4.04
200	95.4	2.55	94.7	2.51	92.5	4.32	94.6	3.16
300	96.5	2.04	96.4	2.09	95.1	2.88	95.1	2.84
400	97.6	1.39	97.4	0.39	97.1	1.67	95.8	2.41
500	98.5	0.88	98.1	0.79	97.5	1.44	96.3	2.14
600	98.9	0.65	98.4	0.65	98.3	0.98	96.5	1.99
700	99.2	0.56	98.9	0.61	98.9	0.84	96.8	1.86
5N HCl	–	139.5	–	139.5	–	139.5	–	139.5
200	87.5	17.5	77.1	31.9	69.4	42.6	63.4	51.1
300	91.3	12.2	83.2	22.3	77.3	31.7	71.7	39.5
500	95.1	6.97	91.2	12.3	87.9	16.8	82.6	24.2
700	98.1	2.67	95.7	5.94	92.9	9.89	92.1	11.1
1000	99.8	0.46	99.6	0.56	98.8	1.67	98.3	2.32

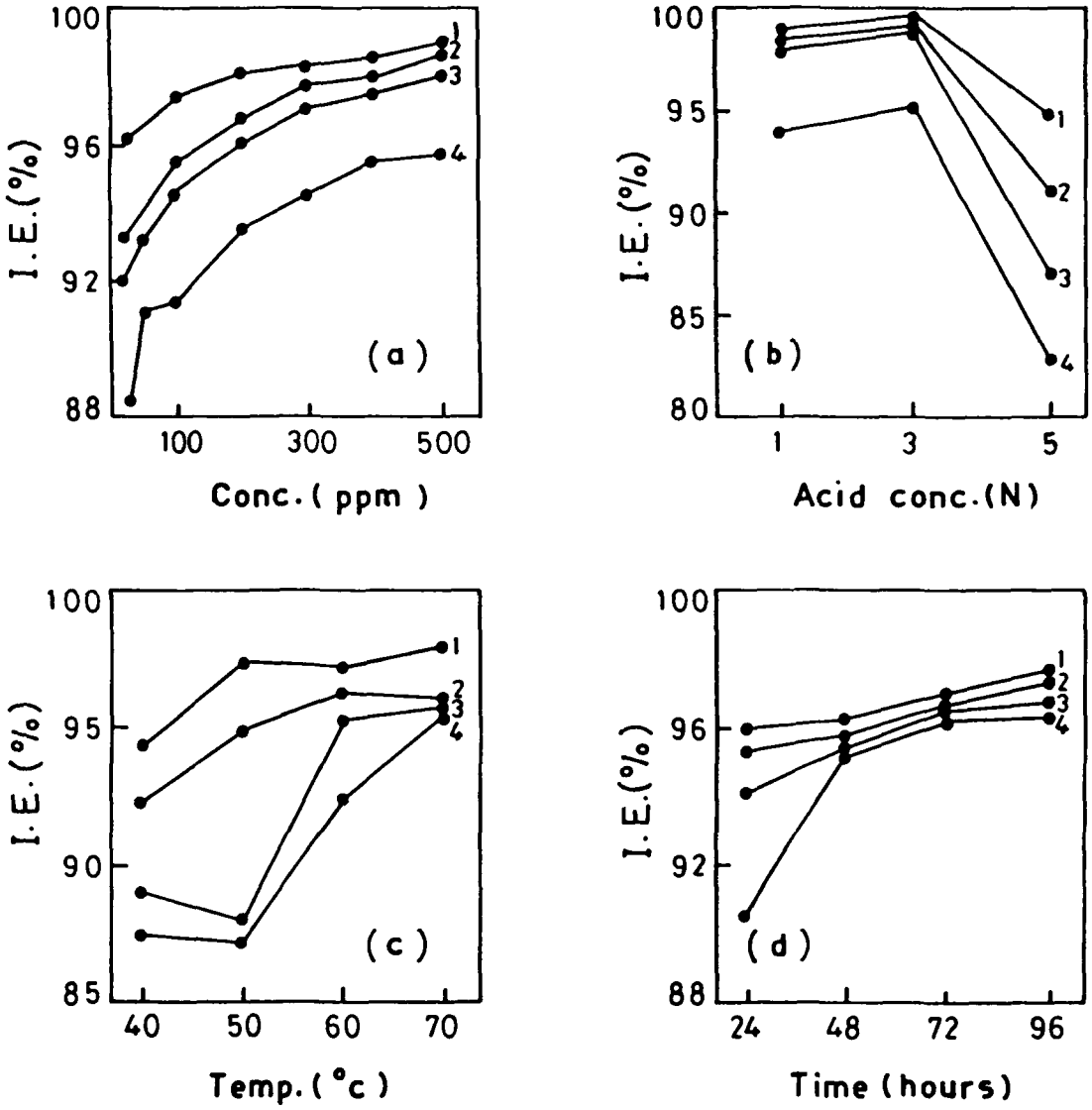


FIGURE 3.3.1 Variation of inhibition efficiency with :

(a) Inhibitor concentration (ppm) at 40°C in 1N HCl

(b) Concentration (N) of HCl cotaining 500 PPM of inhibitor at 40°C

(c) Temp. (°C) in 1 N HCl cotaining 500 PPM of inhibitor

(d) Immersion time (hours) at room temp. 35 ± 2°C in 1N HCl containing 500 ppm concentration of inhibitors

1. APDTB 2. TPDTB 3. DPDTB 4. CPDTB

The inhibition efficiency of all the substituted dithiobiurets is found to decrease with the increase in acid concentration from 1N to 5N HCl [Figure 3.3.1 (b)]. This is due to the desorption of inhibitor molecule at high acid concentration as compared to that of low acid concentration.

The effect of temperature on the inhibition efficiency of dithiobiurets in 1N HCl is shown in Figure 3.3.1 (c). It has been found that I E increases with the increase of temperature from 40 - 70° C. The increase in inhibition efficiency may be attributed to the chemisorption of dithiobiurets on the mild steel surface. The effect of immersion time on inhibition efficiency has been shown in Figure 3.3.1 (d). It is clear that inhibition efficiency of dithiobiurets increases with immersion time due to the formation of barrier film, which prevents the attack of acid on metal surface.

The values of inhibition efficiency for the specific concentrations of inhibitor in combination with KI in different concentration of HCl at 40° C are given in Table 3.3.3.

Table 3.3.3- Inhibition efficiencies of substituted dithiobiurets obtained from weight loss measurements in absence and presence of KI.

Inhi. Conc. (ppm)	KI Conc. (%)	I E (%)			
		APDTB	TPDTB	DPDTB	CPDTB
1N HCl					
15	–	81.5	72.9	69.1	56.7
15	0.02	91.7	90.1	89.8	87.8
20	–	83.9	79.1	75.9	71.3
20	0.02	97.6	96.1	95.7	94.4
3N HCl					
25	–	78.5	72.1	60.3	55.9
25	0.05	91.6	88.1	83.3	77.1
50	–	85.9	84.4	72.2	67.4
50	0.05	96.4	94.3	93.8	93.1
5N HCl					
100	–	83.9	74.5	58.5	51.9
100	0.1	95.1	86.6	75.2	73.6
200	–	87.5	77.1	69.4	63.4
200	0.1	97.7	95.8	93.1	90.8

It is found that the addition of 0.2 % KI to 1N HCl containing 15 ppm of dithiobiurets increases inhibition efficiency by more than 10 % due to synergism. The synergistic effect has also been observed in 3N and 5N HCl.

The value of I E and C R obtained in absence and presence of different concentration of substituted dithiobiurets in 5N HCl at 70° C for 30 minutes have been shown in Table 3.3.4 . All these substituted dithiobiurets exhibit more than 95 % I E at 2000 ppm concentration. Their I E further increased on the addition of KI.

Table 3.3.4- Corrosion parameters obtained from weight loss studies for mild steel in 5N HCl containing different concentrations of substituted dithiobiurets compounds with and without KI (0.25 %) at 70°C for 30 minutes.

Inhi. Conc. (PPM)	APDTB		TPDTB		DPDTB		CPDTB	
	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)
5N HCl	–	1522.6	–	1522.6	–	1522.6	–	1522.6
500	87.6	188.4	46.4	816.7	40.7	903.4	37.6	949.9
1000	98.7	19.2	98.8	17.4	90.4	145.4	89.7	156.3
1500	98.9	16.5	98.9	17.1	95.1	75.6	94.8	78.9
2000	99.2	14.8	99.1	16.6	98.2	27.8	96.9	46.5
500+ 0.25 %KI	96.4	55.5	81.1	28.7	73.3	406.1	72.1	406.1
1000+ 0.25%KI	99.3	13.8	98.4	60.1	95.6	66.6	95.4	69.8

3.3.1.1 ADSORPTION ISOTHERM

The adsorption of all substituted dithiobiurets in 1 - 5N HCl was confirmed by plotting the θ (surface coverage) vs log C (concentration). The straight line obtained in all cases showed that these compounds follow Temkin's adsorption isotherm [Figure 3.3.2 (a - c)].

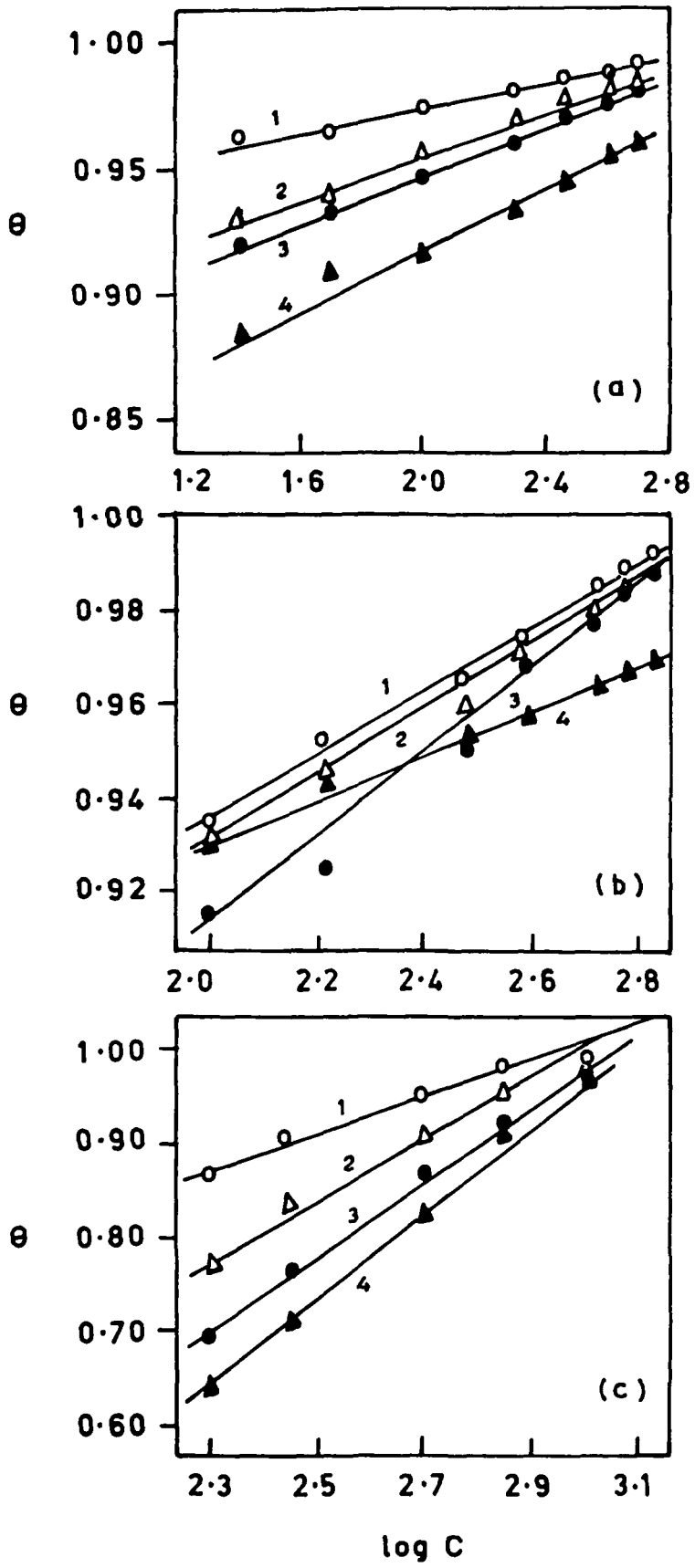


FIGURE 3.3.2 Temkin's adsorption isotherm plots for mild steel in (a) 1 N (b) 3 N (c) 5N HCl containing different concentrations of substituted dithiobiurets :–

1. APDTB 2. TPDTB 3. DPDTB 4. CPDTB

3.3.2 POTENTIODYNAMIC POLARIZATION STUDIES

Both the anodic and cathodic polarization behavior of mild steel in 1 - 5N HCl in absence and presence of substituted dithiobiurets are shown in Figure 3.3.3 - 3.3.6. Various electrochemical corrosion parameters calculated from Tafel plots such as corrosion current density (I_{corr}), Corrosion potential (E_{corr}), Tafel slope constants (b_c and b_a) and inhibition efficiency (I E) are given in Table 3.3.5 - 3.3.7. The results show that the I_{corr} values decrease considerably in the presence of different concentrations of inhibitors. The maximum decrease in I_{corr} value is obtained at 500, 700 and 1000 ppm in 1N, 3N and 5N HCl respectively. The electrochemical polarization curves of TPDTB and CPDTB show predominantly cathodic nature of inhibition in all acidic solutions. E_{corr} values do not change significantly in presence of DPDTB and APDTB in 1 - 5N HCl showing that they are mixed type inhibitors. There is no appreciable change in b_c and b_a value in 1 - 5N HCl solutions containing different concentrations of dithiobiurets, thereby showing that inhibition of corrosion takes place by blocking the active sites of the corrosion reaction. All the compounds follow the same order of inhibition efficiencies as obtained by weight loss studies. The addition of small amount of KI to 5N HCl solution containing 200 ppm of inhibitor further bring down the I_{corr} values significantly due to synergistic effect.

3.3.3 ELECTROCHEMICAL IMPEDANCE STUDIES

Various impedance parameters such as charge transfer resistance (R_t), double layer capacitance (C_{dl}), corrosion current density (I_{corr}) and inhibition efficiency (IE) obtained from Nyquist plot in 1N HCl in absence and presence of different concentrations of substituted dithiobiurets are given in Table 3.3.8. It is clearly seen from Figures 3.3.7(a - d) that the presence of dithiobiurets increase R_t values and decrease C_{dl} and I_{corr} values.

Table 3.3.5- Potentiodynamic electrochemical parameters for mild steel in 1N HCl containing different concentrations of substituted dithiobiurets at 35°C.

Inhi. Conc. (ppm)	I_{corr} (μAcm^{-2})	E_{corr} (mv)	b_c (mv dec^{-1})	b_a (mv dec^{-1})	IE (%)
1N HCl	350	-554	130	60	--
APDTB					
50	72	-558	120	56	79.43
100	60	-562	130	60	82.86
300	55	-564	110	46	84.29
400	47	-570	110	44	86.57
500	42	-576	130	64	88.00
TPDTB					
50	88	-552	128	54	74.86
100	76	-550	130	60	78.29
300	62	-564	120	58	82.29
400	52	-552	124	54	85.14
500	50	-556	136	68	85.71
DPDTB					
50	80	-560	132	54	77.14
100	72	-562	134	58	79.43
300	64	-568	140	60	81.71
400	58	-570	140	64	83.43
500	56	-572	144	68	84.00
CPDTB					
50	90	-550	130	58	74.29
100	86	-556	128	60	75.43
300	70	-558	130	58	80.00
400	65	-550	130	62	81.43
500	60	-552	150	68	82.86

Table 3.3.6- Potentiodynamic electrochemical parameters for mild steel in 3N HCl containing different concentrations of substituted dithiobiurets at 35°C.

Inhi. Conc. (ppm)	I_{corr} (μAcm^{-2})	E_{corr} (mv)	b_c (mv dec^{-1})	b_a (mv dec^{-1})	IE (%)
3N HCl	1200	-568	126	60	--
APDTB					
100	120	-576	120	60	90.00
300	110	-578	110	50	90.83
500	98	-580	118	56	91.83
700	80	-586	110	48	99.33
TPDTB					
100	126	-562	116	56	89.50
300	110	-566	124	60	90.83
500	100	-568	110	52	91.67
700	84	-570	120	62	93.00
DPDTB					
100	130	-572	110	50	89.17
300	120	-578	110	50	90.00
500	84	-580	128	58	93.00
700	82	-588	120	60	93.17
CPDTB					
100	120	-566	110	50	90.00
300	100	-564	120	54	91.67
500	90	-570	122	58	92.50
700	88	-568	120	60	92.67

Table 3.3.7- Potentiodynamic electrochemical parameters for mild steel in 5N HCl containing different concentrations of substituted dithiobiurets with and without (0.25%) KI at 35°C.

Inhi. Conc. (ppm)	I_{corr} (μAcm^{-2})	E_{corr} (mv)	b_c ($mv\ dec^{-1}$)	b_a ($mv\ dec^{-1}$)	IE (%)
5N HCl	4000	-520	130	80	--
5N HCl +KI	580	-516	130	58	85.50
APDTB					
300	210	-532	120	50	94.75
500	150	-536	110	48	96.25
700	120	-538	120	48	97.00
1000	105	-546	120	58	97.38
300 + KI	90	-546	120	60	97.75
500 + KI	88	-548	110	56	97.80
TPDTB					
300	230	-514	100	42	94.25
500	170	-518	100	44	95.75
700	140	-520	120	54	96.00
1000	120	-522	124	63	96.50
300 + KI	110	-516	120	60	97.25
500 + KI	98	-520	110	58	97.55
DPDTB					
300	360	-528	115	52	91.00
500	350	-530	120	56	91.25
700	310	-534	110	58	92.25
1000	280	-540	124	60	93.00
300 + KI	160	-546	122	58	96.00
500 + KI	140	-550	124	62	96.50
CPDTB					
300	520	-518	124	44	87.00
500	400	-524	126	44	90.00
700	340	-520	124	46	91.50
1000	260	-522	120	48	93.50
300 + KI	190	-520	120	50	95.25
500 + KI	120	-522	116	55	97.00

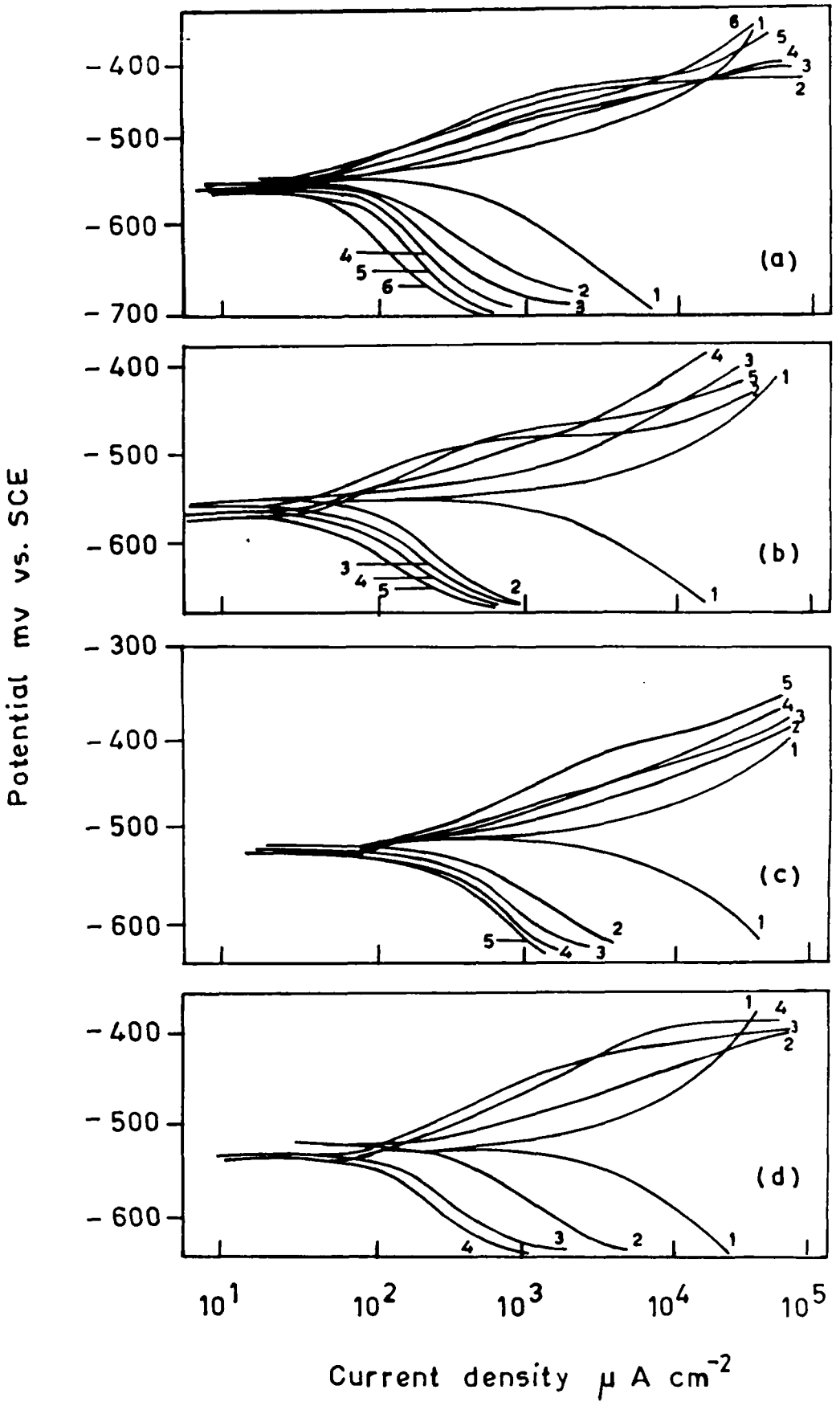


FIGURE 3.3.3 Potentiodynamic polarization curves for mild steel containing different concentrations of APDTB in : –

(a) 1N HCl : 1. Blank 2. 50 ppm 3. 100 ppm 4. 300 ppm 5. 400 ppm 6. 500 ppm
(b) 3N HCl : 1. Blank 2. 100 ppm 3. 300 ppm 4. 500 ppm 5. 700 ppm
(c) 5N HCl : 1. Blank 2. 300 ppm 3. 500 ppm 4. 700 ppm 5. 1000 ppm
(d) 5N HCl : 1. Blank 2. 5N HCl + KI 3. 300 ppm + KI 4. 500 ppm + KI

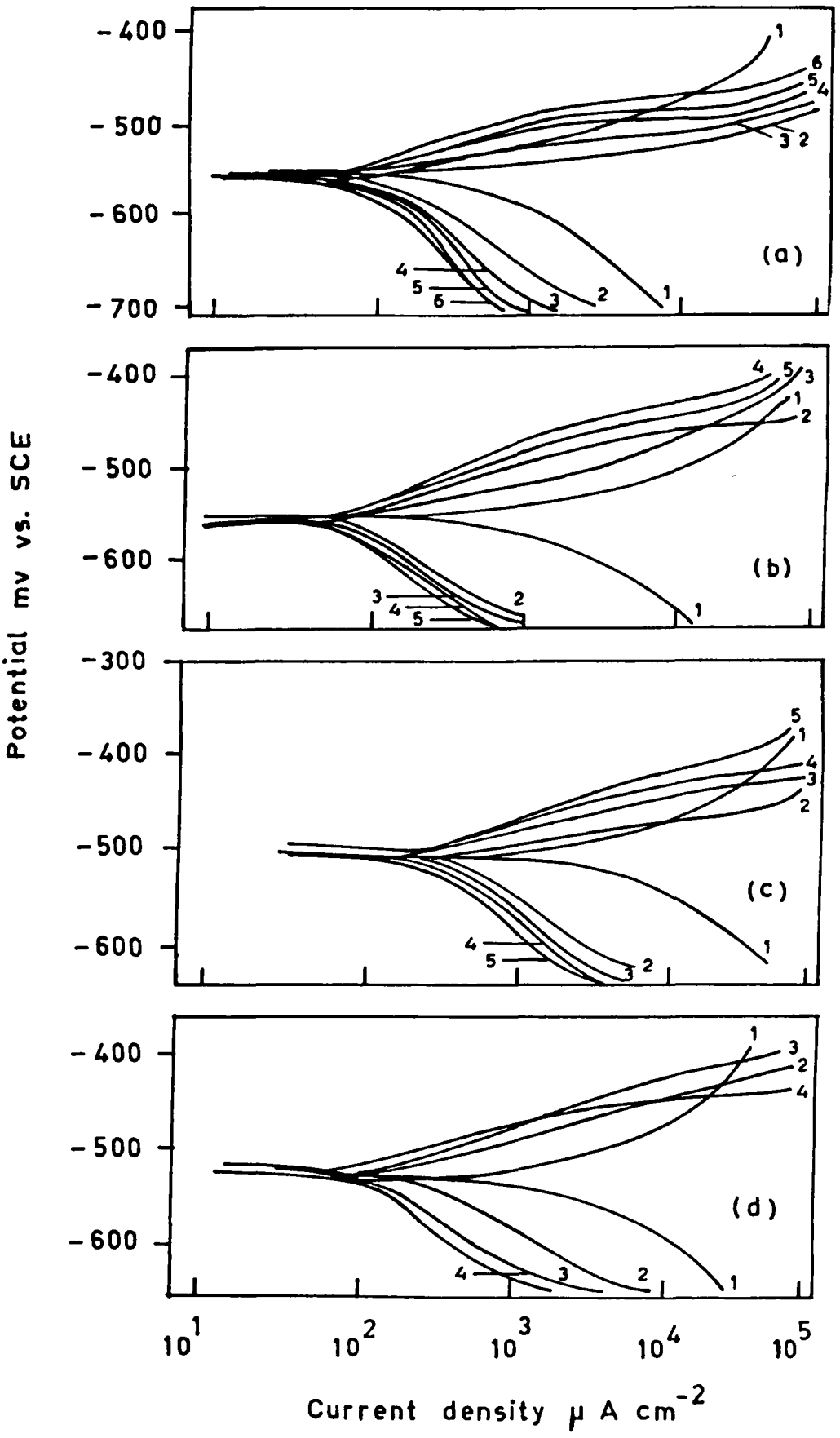


FIGURE 3.3.4 Potentiodynamic polarization curves for mild steel containing different concentrations of TPDTB in : –

(a) 1N HCl :	1. Blank	2. 50 ppm	3. 100 ppm	4. 300 ppm	5. 400 ppm	6. 500 ppm
(b) 3N HCl :	1. Blank	2. 100 ppm	3. 300 ppm	4. 500 ppm	5. 700 ppm	
(c) 5N HCl :	1. Blank	2. 300 ppm	3. 500 ppm	4. 700 ppm	5. 1000 ppm	
(d) 5N HCl :	1. Blank	2. 5N HCl + KI	3. 300ppm + KI	4. 500 ppm + KI		

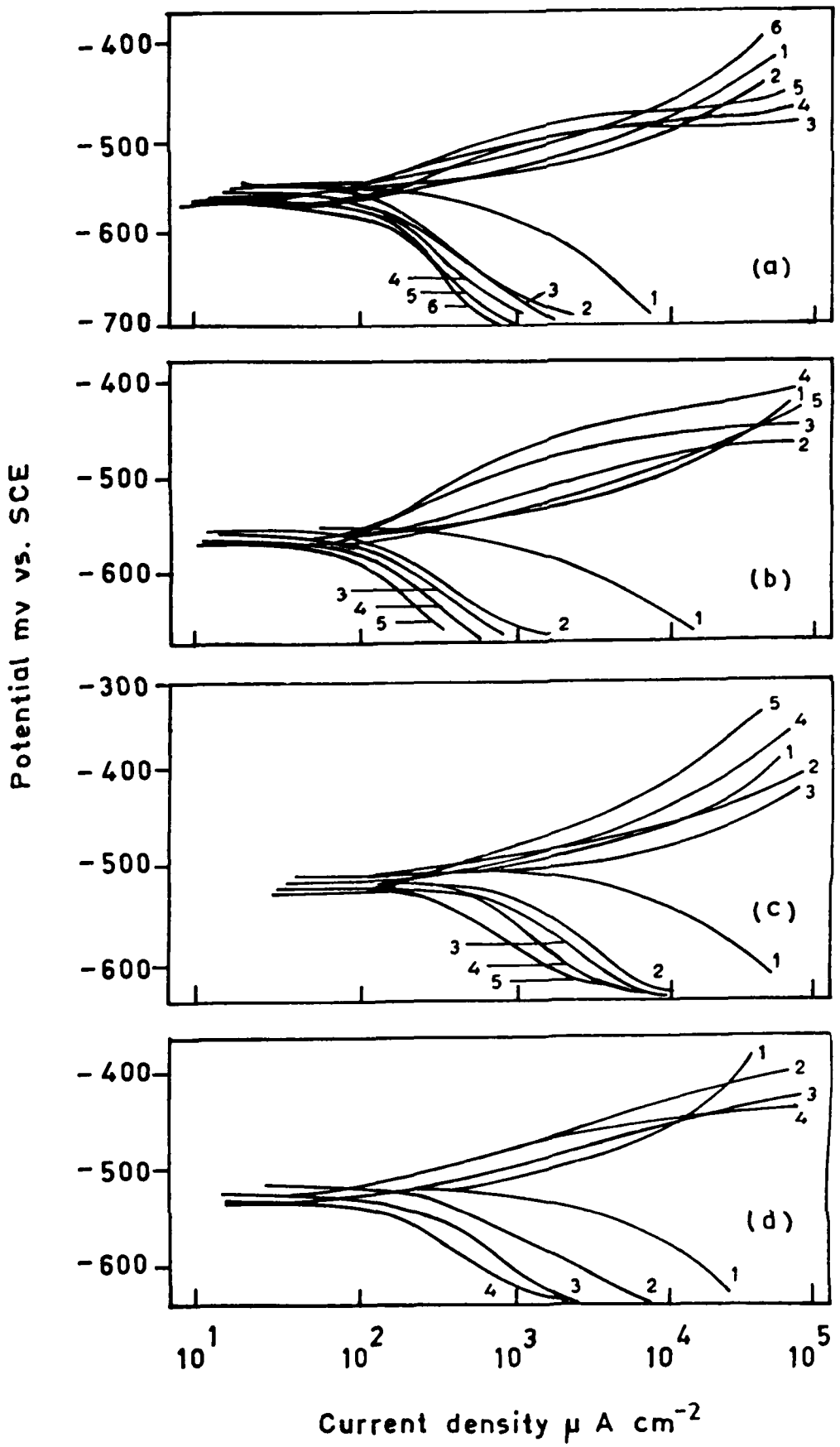


FIGURE 3.3.5 Potentiodynamic polarization curves for mild steel containing different concentrations of DPDTB in : –

(a) 1N HCl : 1. Blank 2. 50 ppm 3. 100 ppm 4. 300 ppm 5. 400 ppm 6. 500 ppm
(b) 3N HCl : 1. Blank 2. 100 ppm 3. 300 ppm 4. 500 ppm 5. 700 ppm
(c) 5N HCl : 1. Blank 2. 300 ppm 3. 500 ppm 4. 700 ppm 5. 1000 ppm
(d) 5N HCl : 1. Blank 2. 5N HCl + KI 3. 300ppm + KI 4. 500 ppm + KI

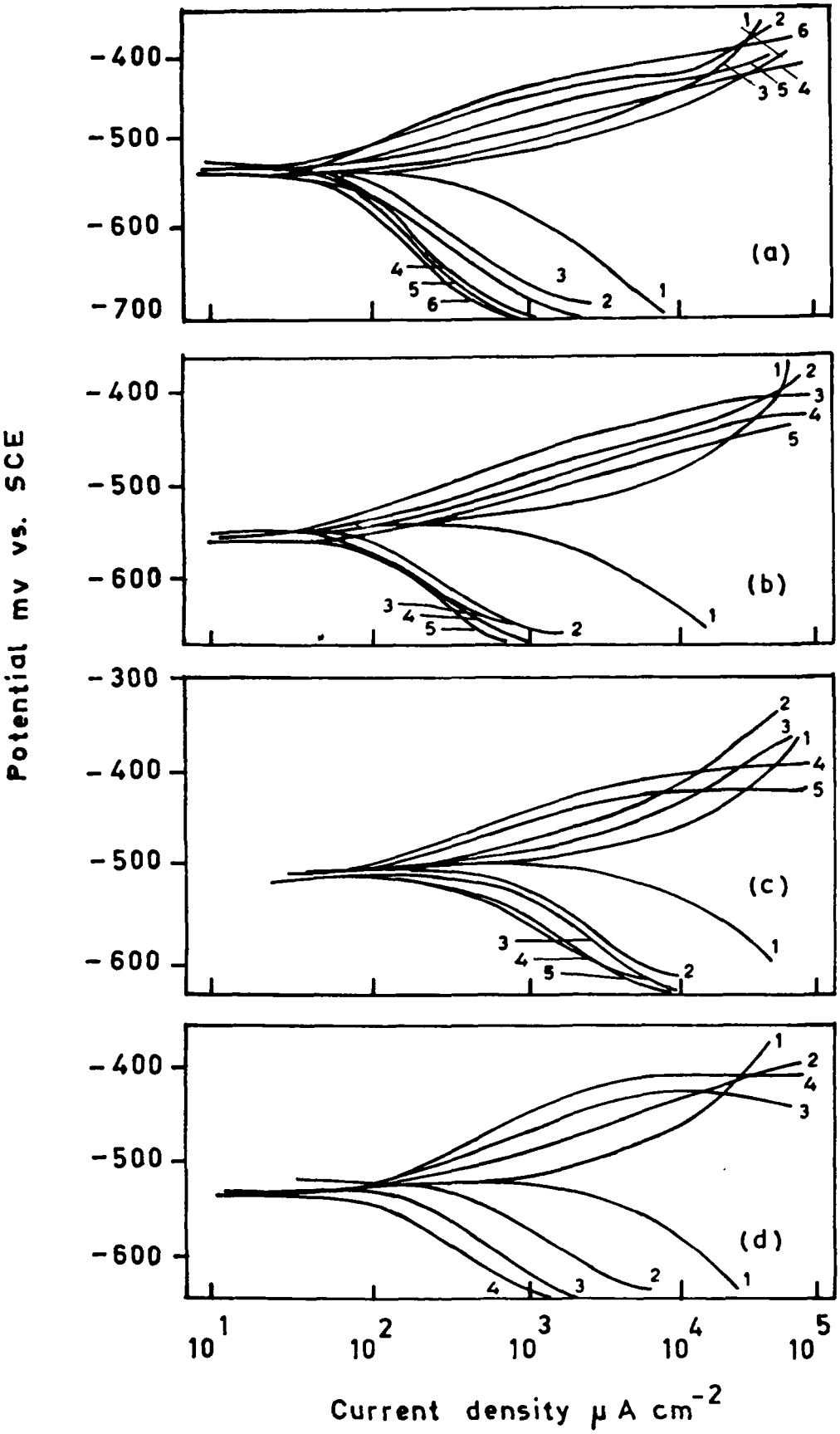


FIGURE 3.3.6 Potentiodynamic polarization curves for mild steel containing different concentrations of CPDTB in : –

(a) 1N HCl : 1. Blank 2. 50 ppm 3. 100 ppm 4. 300 ppm 5. 400 ppm 6. 500 ppm
(b) 3N HCl : 1. Blank 2. 100 ppm 3. 300 ppm 4. 500 ppm 5. 700 ppm
(c) 5N HCl : 1. Blank 2. 300 ppm 3. 500 ppm 4. 700 ppm 5. 1000 ppm
(d) 5N HCl : 1. Blank 2. 5N HCl + KI 3. 300ppm + KI 4. 500 ppm + KI

Table 3.3.8 -Impedance data of mild steel in 1N HCl containing different concentrations of substituted dithiobiurets.

SYSTEM	Inhi. Conc. (ppm)	R_t (Ω cm^2)	C_{dl} (μF cm^{-2})	I_{corr} (μ A cm^{-2})	I E (%)
1N HCl	--	115	12832	155	--
APDTB	300	1500	937	10.05	94.03
	500	2140	845	8.71	94.63
TPDTB	300	1400	1029	12.14	93.83
	500	2000	866	9.86	94.25
DPDTB	300	750	1832	24.35	86.44
	500	900	1729	22.31	87.24
CPDTB	300	650	2350	26.83	83.94
	500	800	1947	25.43	85.63

3.3.4 HYDROGEN PERMEATION STUDIES

Hydrogen permeation curves for mild steel in 1N HCl containing 500 ppm of CPDTB and DPDTB are shown in Figure 3.3.8. The values of percentage reduction and permeation current are given in Table 3.3.9.The results show that both the compounds namely CPDTB and DPDTB bring down the permeation current. The reduction in hydrogen permeation current may be attributed to the adsorption of these compounds on the mild steel surface which prevents permeation of hydrogen into the metal.

Table 3.3.9 - Hydrogen permeation parameters for mild steel in 1N HCl containing 500 ppm of substituted dithiobiurets at 35 ± 2°C

Inhi. Conc. (ppm)	Permeation current (μ A)	Percent reduction (%)
1N HCl	24	--
500 CPDTB	15.2	36.7
500 DPDTB	16.1	33.3

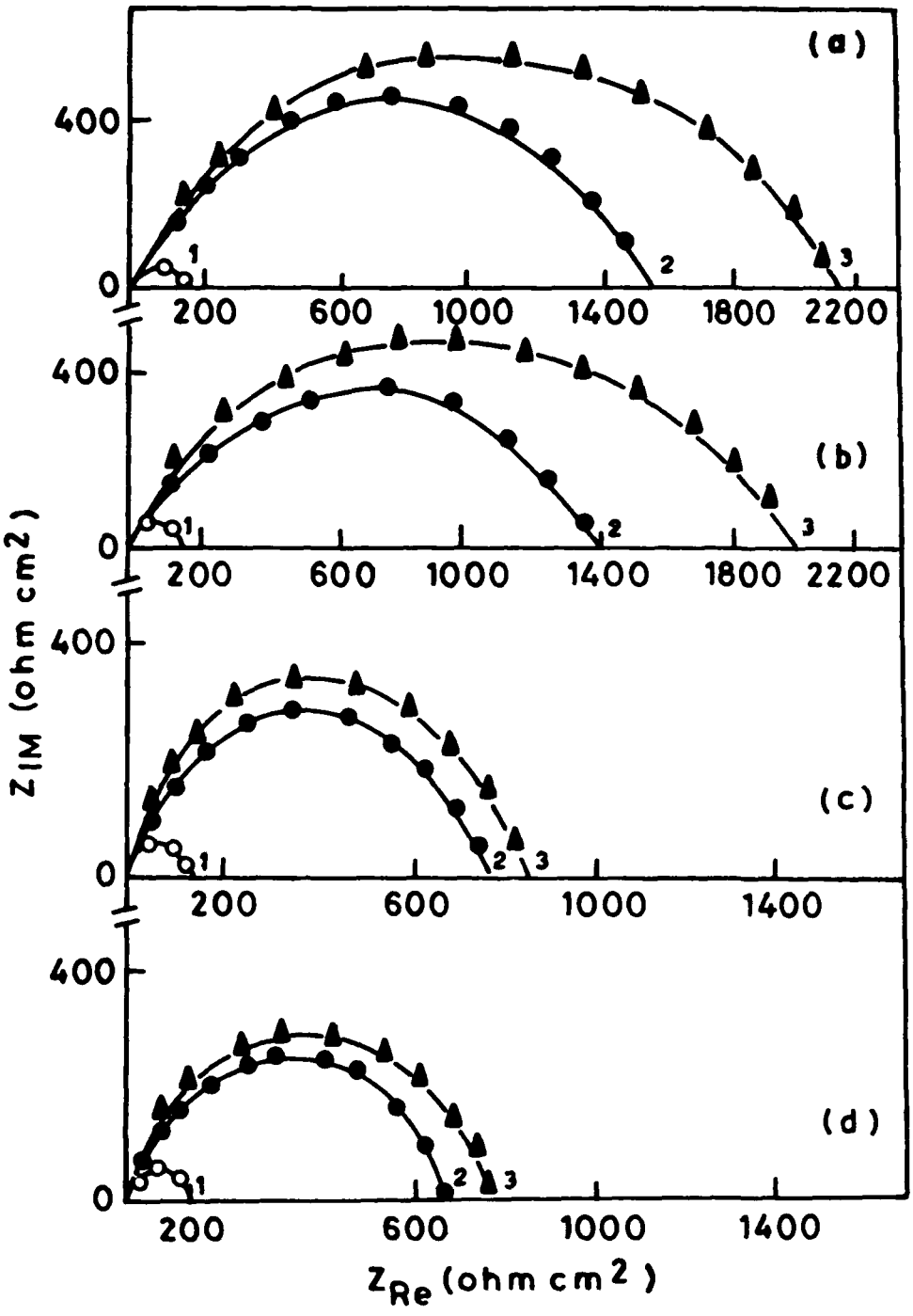


FIGURE 3.3.7 Nyquist plots for mild steel in 1N HCl in absence and presence of different concentrations of substituted dithiobiurets :–

(a) APDTB (b) TPDTB (c) DPDTB (d) CPDTB 1. Blank 2. 300 ppm 3. 500 ppm

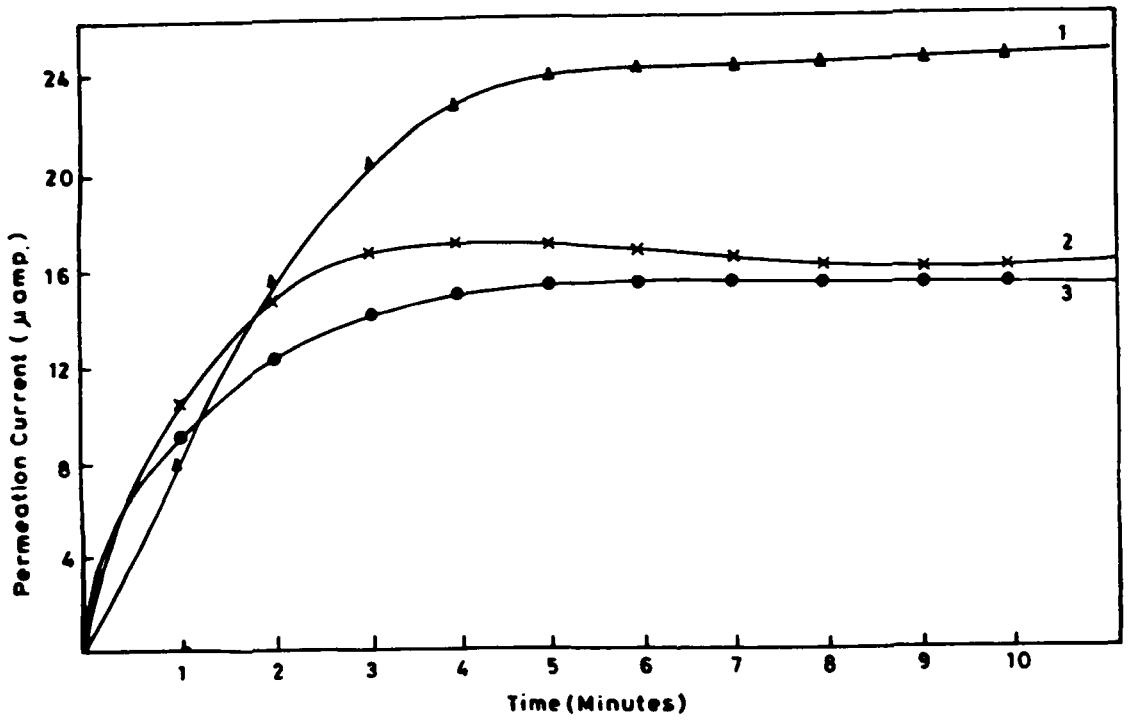


FIGURE 3.3.8 Hydrogen permeation curves for mild steel in 1N HCl in absence and presence of 500 ppm of substituted dithiobiurets .–
1. Blank 2. DPDTB 3. CPDTB

3.3.5 AUGER ELECTRON SPECTROSCOPY

Auger electron spectrum obtained for plain mild steel and mild steel exposed to 1N HCl containing 500 ppm of APDTB and APDTB + KI are shown in Figure 3.3.9 (a - c). The appearance of peaks at 152 and 378 ev respectively indicate the adsorption of APDTB on the metal surface through S and N atoms. The AES spectrum obtained with 300 ppm of APDTB + 0.02 % KI exhibits peaks at 150, 388 and 511 ev, thereby showing the adsorption of the inhibitor through sulphur, nitrogen and iodine on the metal surface. This study also supports the joint adsorption of iodide ions and APDTB.

The values of the atomic concentration of the different elements present on the mild steel surface and the adsorbed inhibitor film are given in Table 3.3.10. The results show the concentration of different elements such as nitrogen, sulphur and iodine on the metal surface.

3.3.6 SCANNING ELECTRON MICROSCOPIC STUDIES

The scanning electron microscopic photographs of plain mild steel, mild steel exposed to 1N HCl and steel exposed to 1N HCl containing 500 ppm of APDTB are shown in Figure 3.3.10 (a - c).These photographs clearly show the smooth plain surface of mild steel exposed to APDTB whereas rough corroded surface of mild steel exposed to 1N HCl, thereby suggesting that the inhibition of corrosion of mild steel takes place due to adsorption of inhibitor on steel surface which prevents the corrosive attacks of acid and keeps the surface smooth.

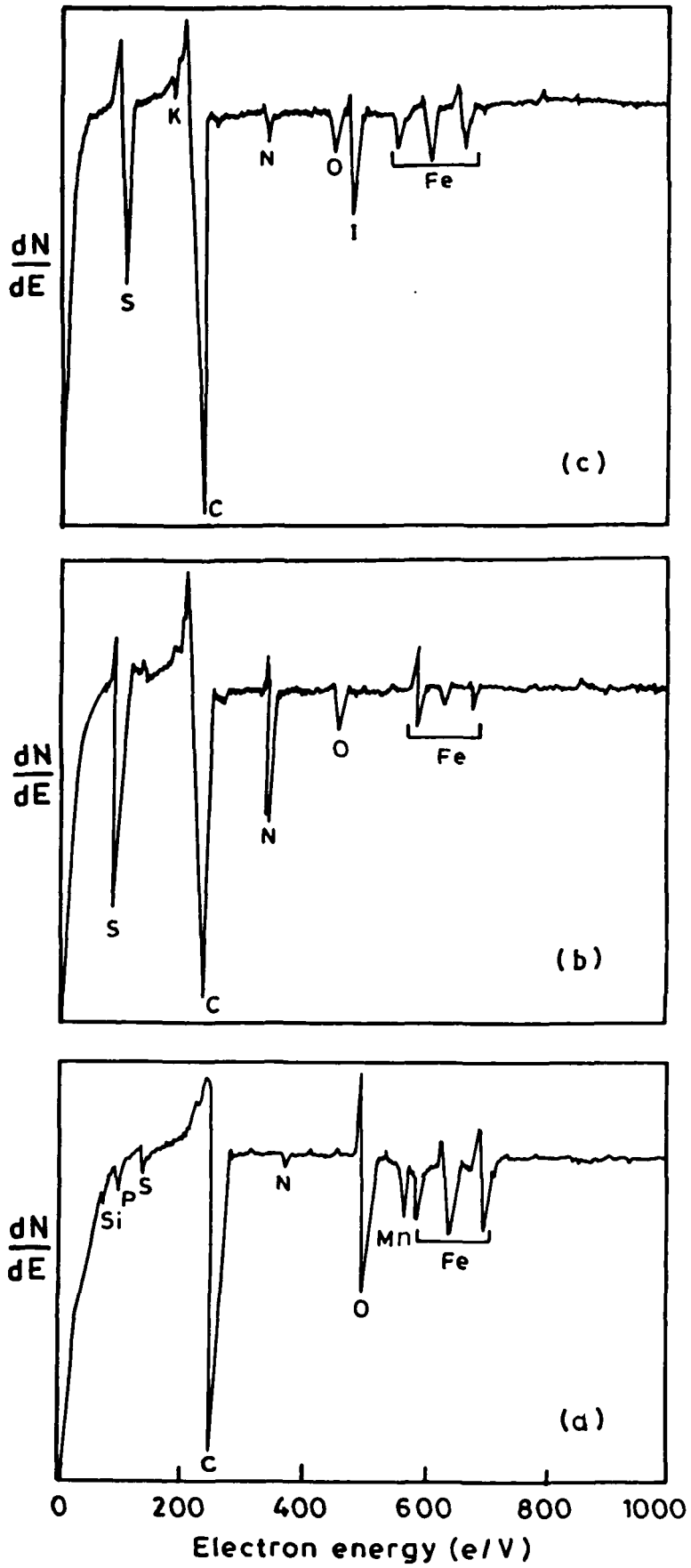
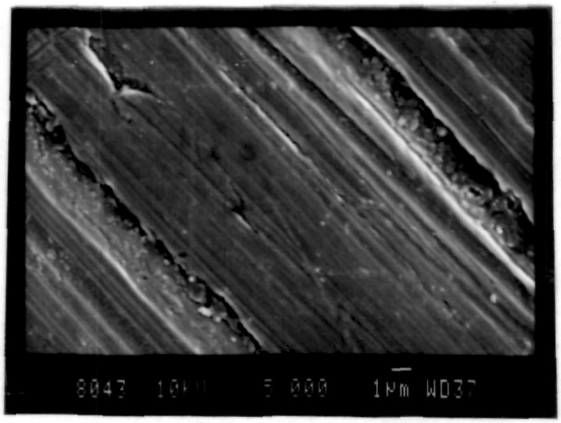


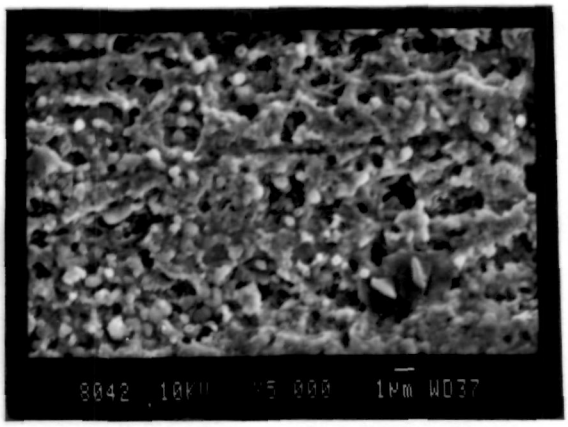
FIGURE 3.3.9 Auger electron spectrum for :–
(a) polished mild steel surface (b) mild steel exposed to APDTB
(c) mild steel exposed to APDTB +KI

Table 3.3.10 - Elemental composition of mild steel obtained from auger electron spectroscopy in presence of APDTB and APDTB + KI in 1N HCl.

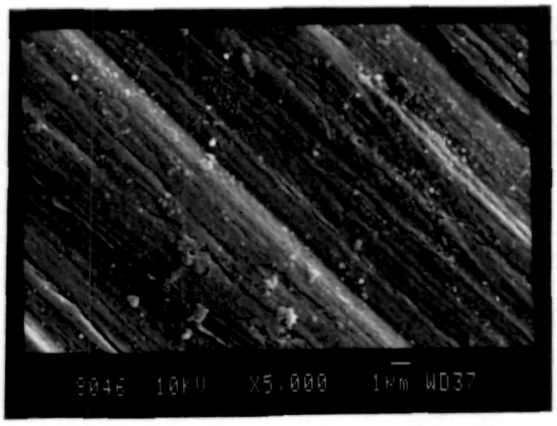
Element	Peak height (mm)	Relative senstivity (S_x)	Composition (%)
Mild steel			
C	122	0.20	57.50
O	73	0.50	13.80
P	10	0.50	1.81
S	9	0.80	1.06
N	4	0.32	1.18
Mn	22	0.23	9.02
Si	2	0.35	0.54
Fe	32	0.20	15.09
APDTB			
C	140	0.20	66.95
S	89	0.80	10.64
N	50	0.32	14.95
Fe	10	0.20	4.78
O	14	0.50	2.68
APDTB+KI			
C	164	0.20	74.84
S	84	0.80	9.58
N	13	0.32	3.71
Fe	6	0.20	2.74
O	5	0.50	0.91
K	7	0.80	0.81
I	26	0.32	7.42



(a)



(b)



(c)

FIGURE 3.3.10 Scanning electron micrographs for :–
(a) Polished mild steel (b) Mild steel in 1N HCl
(c) Mild steel in 1N HCl + 500 ppm APDTB

3.3.7 CONCLUSIONS

The main conclusions drawn from these studies are :—

1. All of the substituted dithiobiurets show good inhibition efficiency in all acidic solution (1 - 5 N HCl).

2. The inhibition efficiencies of all substituted dithiobiurets follow the order :–

   APDTB > TPDTB > DPDTB > CPDTB

3. The IE of all compounds increases with the increase in inhibitor concentration, temperature and immersion time, whereas decreases with the increase in acid concentration.

4. The inhibition efficiencies of all the investigated compounds increase on the addition of K I due to synergistic effect.

5. The adsorption of all these compounds on the mild steel from the acidic solutions obeys Temkin's adsorption isotherm.

6. The potentiodynamic polarization study reveals that APDTB and DPDTB behave as mixed inhibitors whereas TPDTB and CPDTB act as predominantly cathodic inhibitors.

7. Electron impedance spectroscopic studies show that in presence of dithiobiurets R_t values increase while C_{dl} and I_{corr} values decrease.

8. Both the tested compounds namely CPDTB and DPDTB bring down hydrogen permeation current.

9. AES analysis confirms the adsorption of APDTB on mild steel surface through nitrogen and sulphur atoms and also supports synergism.

10. SEM micrographs of mild steel exposed to inhibitor APDTB solution show smooth surface.

SECTION A

THIOCARBOHYDRAZIDES : A NOVEL CLASS OF ACID CORROSION INHIBITORS

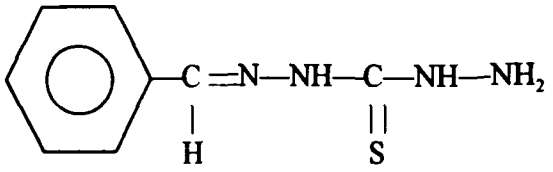
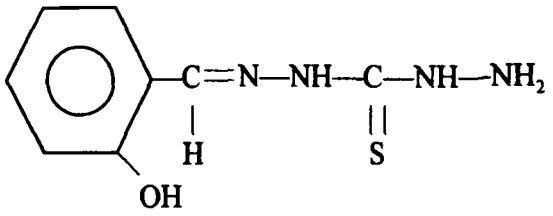
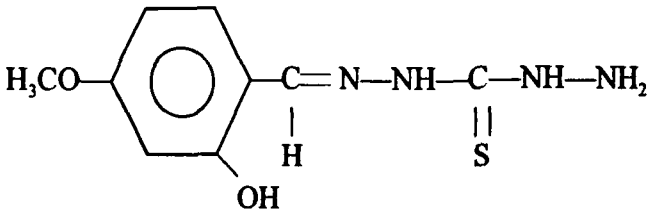
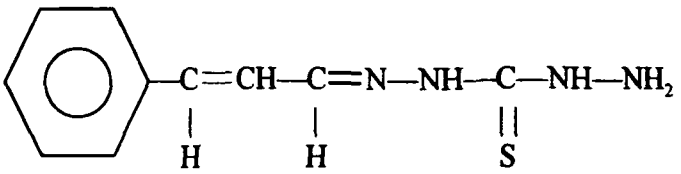
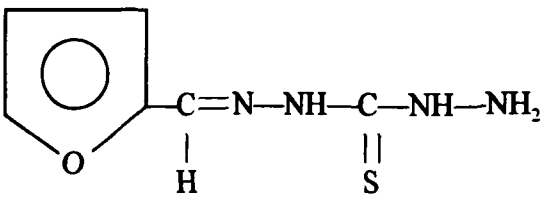
A perusal of literature revealed that aldehydes are effective corrosion inhibitors [47 - 49]. Turbina et. al. [50] have observed that condensation products of p- anisidines and benzaldehyde give higher inhibition efficiency than that of the benzaldehyde and p- anisidine alone. Five new triazoles synthesized by the condensation of aromatic aldehydes and mercapto - triazole have been evaluated for their inhibiting action of corrosion of mild steel in 15 % boiling HCl [51]. Some of these triazole derivatives have shown more than 95 % inhibition efficiency. A few more condensation products were synthesized in our laboratory and their inhibition action was evaluated in acid medium on corrosion of mild steel. These include condensation products of 2 - amino benzothiazole with aldehydes [52], 2 - amino - 4 - mercapto triazole with salicylaldehyde [53] and 2 - amino - 4 - phenylthiazoles with aldehydes [54] to exhibit inhibiting behavior.

In view of the excellent performance of the condensation products as corrosion inhibitors five compounds namely, 1 - benzylidene - 3 - thiocarbohydrazide (BTCH), 1 - salicylidine - 3 - thiocarbohydrazide (STCH), 1 - vanillidene - 3 - thiocarbohydrazide (VTCH), 1 - cinnamylidene - 3 - thiocarbohydrazide (CTCH)and 1 - furfurylidene - 3 - thiocarbohydrazide (FTCH) were synthesized by condensing thiocarbohydrazide with aldehydes such as benzaldehyde, salicyldehyde, vanillin, cinnamaldehyde and furfuraldehyde and their inhibitive action on corrosion of mild steel in 1N, 3N and 5N HCl has been investigated employing weight loss and lectrochemical methods. AES and SEM techniques have also been used to characterize the nature and composition of the inhibitive film. Molecular structure and other details of the inhibitors are given in Table 3.4.1.

3.4.1 WEIGHT LOSS STUDIES

The weight loss measurements were conducted in 1N, 3N and 5N HCl at 40° C temperature for three hours. The corrosion inhibition tests were also conducted in 1N HCl at different temperatures (40 - 70°C) and different immersion period

TABLE 3.4.1 NAME AND STRUCTURAL FORMULAE OF THE INHIBITORS USED

S.No.	STRUCTURAL FORMULA	DESIGNATION AND ABBRIVIATION
1		1-benzylidene-3-thiocarbohydrazide (BTCH)
2		1-salicylidene-3-thiocarbohydrazide (STCH)
3		1-vanillidene-3-thiocarbohydrazide (VTCH)
4		1-cinnamylidene-3-thiocarbohydrazide (CTCH)
5		1-furfurylidene-3-thiocarbohydrazide (FTCH)

(24 - 96 hours). The Various corrosion parameters obtained from weight loss studies such as percentage inhibition efficiency (I E) and corrosion rate (CR) for these compounds in 1N, 3N and 5N HCl are given in Table 3.4.2. It is seen from the table that the inhibition efficiency for all these compounds increases with the increase in concentration [Figure 3.4.1 (a)]. The maximum inhibition efficiency of these compounds were found at 500, 700 and 1000 ppm in 1N, 3N and 5N HCl respectively.

The inhibition efficiencies for these thiocarbohydrazides in 1 - 5N HCl solution at all temperatures followed the order:–

Table 3.4.2 - Corrosion parameters obtained from weight loss measurements for mild steel in 1N, 3N and 5N HCl containing different concentrations of substituted thiocarbohydrazides at 40°C for 3 hours.

Inhi. Conc. (PPM)	CTCH		VTCH		STCH		FTCH		BTCH	
	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)
1N HCl	–	16.81	–	16.81	–	16.81	–	16.81	–	16.81
25	90.6	1.57	90.1	1.57	88.4	1.95	86.7	2.23	83.7	2.69
50	92.5	1.25	91.7	1.39	90.9	1.53	89.5	1.76	86.2	2.32
100	94.8	0.88	93.4	1.11	93.1	1.16	91.9	1.35	89.8	1.71
200	97.2	0.46	94.8	0.88	95.2	0.83	93.7	1.07	91.7	1.39
300	97.5	0.41	96.9	0.61	95.9	0.69	94.5	0.93	93.7	1.06
400	98.6	0.23	97.8	0.37	96.8	0.51	95.3	0.79	94.2	0.94
500	99.2	0.13	98.6	0.23	98.1	0.32	96.7	0.56	95.6	0.74
3N HCl	–	57.8	–	57.8	–	57.8	–	57.8	–	57.8
100	89.7	5.94	85.5	8.35	83.5	9.51	80.7	11.1	77.4	13.2
200	93.9	3.48	90.1	5.71	87.9	7.01	84.5	8.96	82.6	10.1
300	95.1	2.87	91.7	4.78	89.5	6.08	87.9	7.01	86.9	7.56
400	97.9	1.16	92.9	4.08	90.3	5.61	89.3	6.18	88.5	6.64
500	98.6	0.83	93.8	3.57	92.7	4.22	91.9	4.69	90.4	5.52
600	98.8	0.69	93.2	3.94	93.2	4.04	92.7	4.23	91.3	5.01
700	99.1	0.55	93.9	3.48	93.7	3.66	93.7	3.62	92.8	4.13
5N HCl	–	139.5	–	139.5	–	139.5	–	139.5	–	139.5
200	97.1	3.99	84.1	22.2	80.6	27.1	70.8	40.7	69.2	43.2
300	98.3	2.32	85.2	20.7	84.1	22.2	77.6	31.3	75.7	33.9
500	98.6	1.99	92.1	11.1	88.2	16.7	86.8	18.5	84.4	21.7
700	98.9	1.48	94.2	8.12	90.9	12.5	90.2	13.7	87.7	17.2
1000	99.6	0.55	98.4	2.22	95.7	5.94	96.5	4.83	94.5	7.71

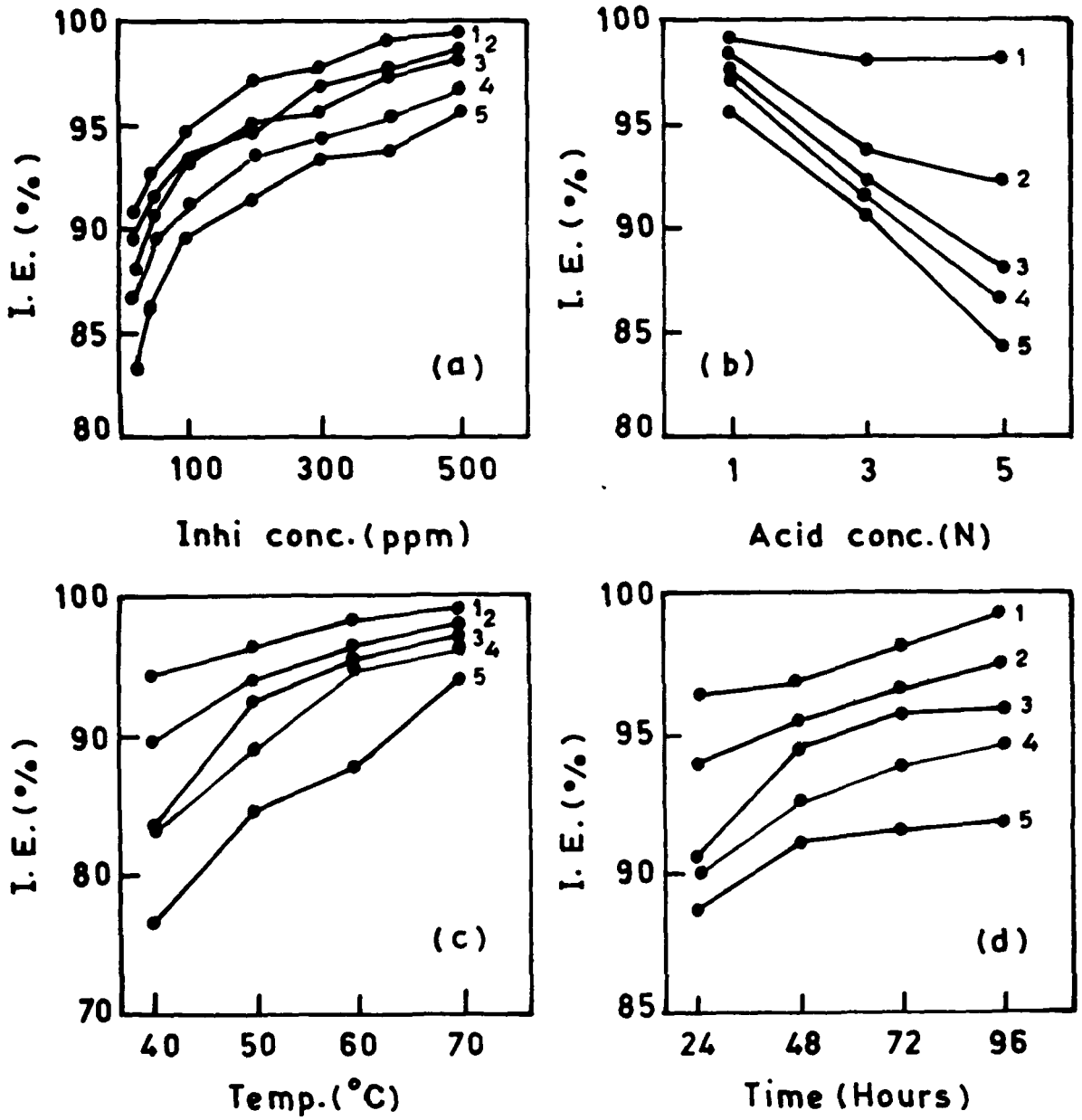


FIGURE 3.4.1 Variation of inhibition efficiency with –

(a) Inhibitor concentration (ppm) at 40°C in 1N HCl

(b) Concentration (N) of HCl cotaining 500 PPM of inhibitor at 40°C

(c) Temp (°C) in 1 N HCl cotaining 500 PPM of inhibitor

(d) Immersion time (hours) at room temp 35 ± 2°C in 1 N HCl containing 500 ppm concentration of inhibitors

1 CTCH 2 VTCH 3 STCH 4 FTCH 5 BTCH

CTCH > VTCH > STCH > FTCH > BTCH

CTCH exhibited highest inhibition efficiency among the studied thiocarbohydrazides which can be explained due to the presence of an additional π bond between carbon atoms – C = C – conjugated to azomethine group (– C=N –). VTCH gives better inhibition efficiency than that for STCH because it contains electron releasing $– OCH_3$ group which is absent in case of STCH. The presence of electron releasing inductive effect of –OH group attached with benzene ring of STCH leads to greater adsorption of STCH than FTCH and thereby corrosion inhibition.

In case of FTCH presence of furan nucleus having oxygen atom with lone pairs of electrons facilitates greater adsorption of FTCH on metal surface as compared to BTCH which leads to more inhibition of corrosion. The adsorption of BTCH on the metal surface can be explained as follows :–

1. π electron of the benzene rings and – C = N – group can interact with metal surface.
2. Lone pairs of electrons present on S or N atoms can interact with metal surface.
3. The absence of conjugated double bonds, $– OCH_3$, – OH and furan nucleus makes it less effective than other compounds under study.

The effect of acid concentration, temperature and immersion time on the inhibition efficiency of these compounds has been shown in Figure 3.4.1(b - d). It is seen that the inhibition efficiency of all the investigated compounds increases from 40 - 70° C due to chemisorption [55]. Increase of acid concentration from 1 - 5N HCl decreases inhibition efficiency of all the investigated compounds VTCH, STCH, FTCH BTCH except for CTCH. It is obvious from the Figure 3.4.1 (d) that inhibition efficiency for all the compounds increases with immersion time. This increase in inhibition efficiency may be attributed to the formation of a barrier film which prevents the attack of acid on metal surface.

The values of inhibition efficiency for specific concentration of inhibitors in combination with K I are given in Table 3.4.3. The results show that the IE of all the

compounds increases on the addition of iodide ions due to synergism. A significant increment in IE values has been seen in 3N and 5N HCl solutions. This suggests that the pronounced synergistic effect takes place in concentrated acid solutions 3N and 5N HCl containing inhibitors.

Table 3.4.3- Inhibition efficiencies of substituted thiocarbohydrazides obtained from weight loss measurements in absence and presence of KI.

Inhibitor Conc. (PPM)	KI Conc. (%)	IE (%)				
		CTCH	VTCH	STCH	FTCH	BTCH
1N HCl						
25	--	90.60	90.10	88.40	86.70	83.70
25	0.02	95.90	95.60	93.90	91.80	90.60
50	--	92.56	91.72	90.94	89.50	86.20
50	0.02	98.60	98.10	97.20	96.70	95.00
3N HCl						
100	--	89.70	85.50	83.50	80.70	77.40
100	0.05	97.10	91.80	91.60	90.70	90.30
300	--	95.16	91.70	89.50	87.90	86.90
300	0.05	98.70	97.60	95.90	91.40	94.50
5N HCl						
200	--	97.10	84.10	80.60	70.80	69.20
200	0.1	98.10	88.90	85.80	83.90	80.80
500	--	98.60	92.10	88.22	86.80	84.40
500	0.1	99.70	96.00	95.80	94.70	93.40

The values of inhibition efficiencies and corrosion rates obtained in the presence of different concentrations of substituted thiocarbohydrazide in 5N HCl at 70° C for 30 minutes are given in Table 3.4.4. CTCH exhibited the highest inhibition efficiency of 99.5 % at a concentration of 3000 ppm while other thiocarbohydrazide showed their maximum inhibition efficiency at 5000 ppm. The inhibition efficiency of all the tested compounds increased nearly by 10 % on the addition of KI due to synergism.

Table 3.4.4- Corrosion parameters obtained from weight loss studies for mild steel in 5N HCl containing different concentrations of subtituted thiocarbohydrazides with and without KI (0.25%) at 70°C for 30 minutes.

Inhi. Conc. (PPM)	CTCH		VTCH		STCH		FTCH		BTCH	
	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)	IE (%)	CR (mmpy)
5N HCl	–	1366.2	–	1366.2	–	1366.2	–	1366.2	–	1366.2
500	99.1	13.7	52.3	725.7	50.1	760.1	49.2	773.8	42.2	880.6
1000	99.2	11.1	80.2	301.7	71.6	432.8	70.1	445.7	80.3	300.2
1500	99.4	9.13	94.3	86.2	90.1	151.7	89.6	158.7	87.2	197.4
2000	99.8	7.04	96.3	55.5	95.6	66.6	94.7	140.8	92.5	115.1
500+KI	99.2	12.9	66.1	540.7	60.8	602.4	64.9	590.7	67.6	510.8
1000+KI	99.4	8.69	92.5	115.1	91.7	126.4	80.2	301.6	85.6	218.9

3.4.1.1 ADSORPTION ISOTHERM

The values of surface coverage (θ) were evaluated from the weight loss data of different inhibitor concentration in 1 - 5N HCl, were plotted against log C (inhibitor concentration). A straight line was obtained in all cases [Figure 3.4.2 a -c)]. These observations suggest that the adsorption of all these compounds on mild steel surface obeys Temkin' s adsorption isotherm.

3.4.2 POTENTIODYNAMIC POLARIZATION STUDIES

The anodic and cathodic polarization behavior of mild steel in 1 - 5N HCl in absence and presence of different concentrations of all substituted thiocarbohydrazides are shown in Figure 3.4.3 - 3.4.7. The electrochemical corrosion parameters calculated from Tafel plots such as corrosion current density (I_{corr}), Corrosion potential (E_{corr}), Tafel slope constants (b_c and b_a) and inhibition efficiency (I E) are given in Table 3.4.5 - 3.4.7. It is evident from these results that I_{corr} values decrease on increasing the concentration of inhibitors. Maximum decrease in I_{corr} value was obtained at 500, 700 and 1000 ppm concentration of inhibitors in 1N, 3N and 5N HCl respectively.

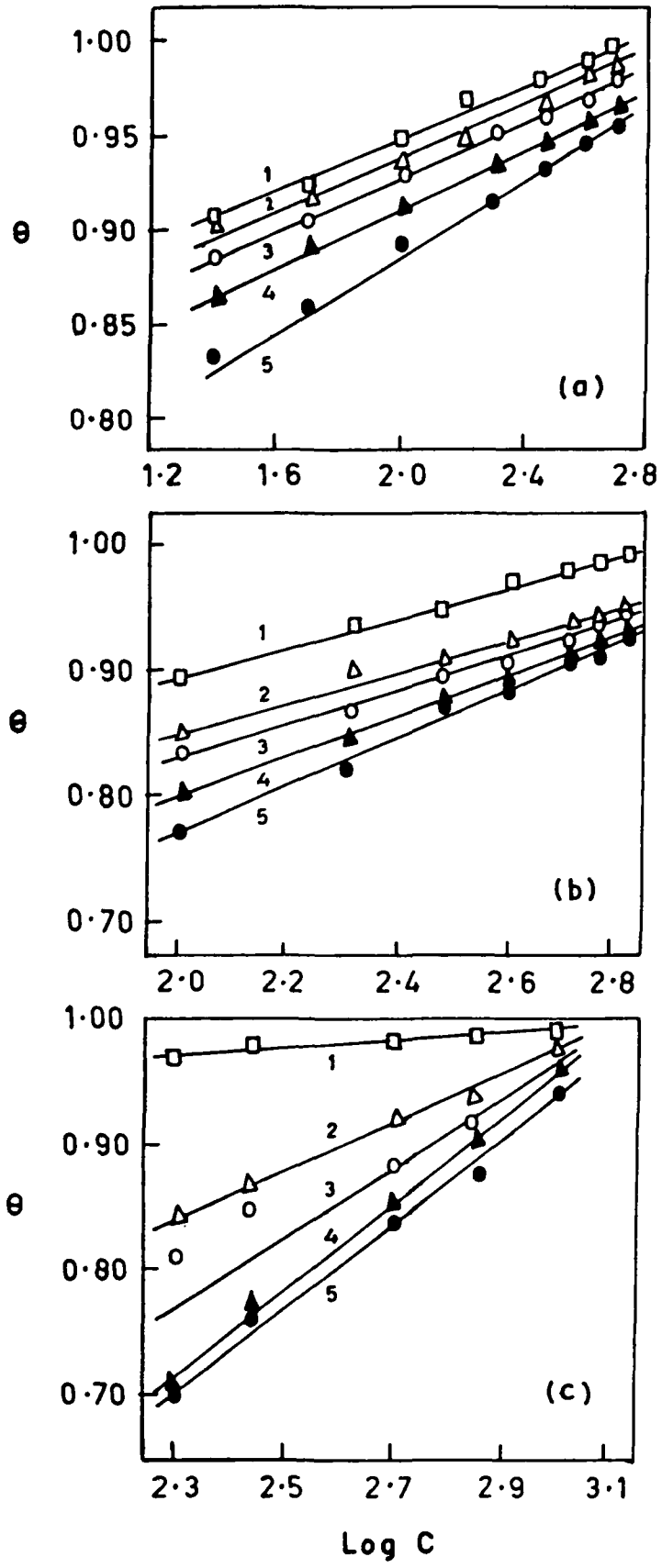


FIGURE 3.4.2 Temkin's adsorption isotherm plots for mild steel in (a) 1 N (b) 3 N (c) 5N HCl containing different concentrations of substituted thiocarbohydrazides
1. CTCH 2. VTCH 3.STCH 4. FTCH 5. BTCH

Table 3.4.5- Potentiodynamic electrochemical parameters for mild steel in 1N HCl containing different concentrations of substituted thiocarbohydrazides at 35°C.

Inhi. Conc. (ppm)	I_{corr} (μAcm^{-2})	E_{corr} (mv)	b_c (mv dec^{-1})	b_a (mv dec^{-1})	IE (%)
1N HCl	350	-554	130	60	–
CTCH					
50	105	-568	130	78	70.00
100	90	-570	110	50	74.29
300	60	-572	126	60	82.86
400	48	-578	120	60	86.29
500	40	-580	120	64	88.57
VTCH					
50	94	-550	126	64	73.14
100	74	-554	130	68	78.86
300	62	-552	132	66	82.29
400	50	-556	136	70	85.71
500	45	-558	120	60	87.14
STCH					
50	140	-552	122	60	60.00
100	110	-554	120	60	60.57
300	90	-550	118	64	74.29
400	58	-552	116	60	83.43
500	44	-556	120	60	87.43
FTCH					
50	160	-562	124	66	54.29
100	125	-570	124	60	64.29
300	105	-578	140	70	70.00
400	80	-580	125	55	77.14
500	64	-584	130	70	81.71
BTCH					
50	160	-552	120	55	54.29
100	125	-550	120	60	64.29
300	109	-554	130	70	68.86
400	90	-552	126	60	74.29
500	74	-556	120	60	78.86

Table 3.4.6- Potentiodynamic electrochemical parameters for mild steel in 3N HCl containing different concentrations of substituted thiocarbohydrazides at 35°C.

Inhi. Conc. (ppm)	I_{corr} (μAcm^{-2})	E_{corr} (mv)	b_c (mv dec^{-1})	b_a (mv dec^{-1})	IE (%)
3N HCl	1200	-568	130	70	–
CTCH					
100	105	-578	133	60	91.25
300	98	-580	128	62	91.83
500	73	-584	118	58	93.92
700	72	-590	110	50	94.00
VTCH					
100	300	-560	130	60	75.00
300	150	-566	130	65	87.50
500	90	-570	134	72	92.50
700	82	-572	130	70	93.17
STCH					
100	200	-566	135	65	83.33
300	160	-568	120	55	86.67
500	120	-564	135	62	90.00
700	100	-570	130	60	91.67
FTCH					
100	360	-578	132	58	70.00
300	240	-580	122	60	80.00
500	180	-584	120	66	85.00
700	160	-596	124	68	86.67
BTCH					
100	390	-566	125	65	67.50
300	300	-570	130	62	75.00
500	260	-568	125	65	78.33
700	200	-570	140	65	83.33

Table 3.4.7- Potentiodynamic electrochemical parameters for mild steel in 5N HCl containing different concentrations of substituted thiocarbohydrazides with and without (0.25%) KI at 35°C.

Inhi. Conc. (ppm)	I_{corr} (μAcm^{-2})	E_{corr} (mv)	b_c (mv dec^{-1})	b_a (mv dec^{-1})	IE (%)
5N HCl	4000	-520	130	80	–
5N HCl + KI	580	-516	130	58	85.50
CTCH					
300	150	-536	128	72	96.25
500	110	-544	130	70	97.25
700	66	-548	130	65	98.35
1000	60	-550	140	70	98.50
300+KI	90	-536	140	78	97.75
500+KI	86	-538	136	70	97.85
VTCH					
300	900	-526	105	55	77.50
500	390	-528	120	70	90.25
700	280	-512	110	60	93.00
1000	180	-510	126	74	95.50
300+KI	130	-522	118	50	96.75
500+KI	120	-524	134	68	97.00
STCH					
300	910	-512	120	62	77.25
500	760	-516	124	70	81.00
700	360	-518	120	65	91.00
1000	220	-520	128	65	94.50
300+KI	120	-524	134	72	97.00
500+KI	110	-526	130	65	97.25

Contd -------

Inhi. Conc. (ppm)	I_{corr} (μAcm^{-2})	E_{corr} (mv)	b_c (mv dec^{-1})	b_a (mv dec^{-1})	IE (%)
FTCH					
300	850	-528	120	70	78.75
500	640	-536	120	50	84.00
700	450	-540	100	54	88.75
1000	320	-550	110	50	92.00
300+KI	160	-532	118	50	96.00
500+KI	140	-538	140	65	96.50
BTCH					
300	880	-522	130	74	78.00
500	640	-520	120	60	84.00
700	480	-522	110	55	88.00
1000	450	-524	120	60	88.75
300+KI	460	-524	124	60	88.50
500+KI	320	-526	104	50	92.00

No appreciable shift in E_{corr} value was observed in case of VTCH, STCH and BTCH, thereby showing that they are mixed inhibitors. CTCH and FTCH shift the E_{corr} to noble direction in acidic solution thereby showing that CTCH and FTCH are predominantly cathodic inhibitors. It is also found that addition of these inhibitors does not change the Tafel slope values significantly indicating that these compounds inhibit corrosion by blocking the active sites of the mild steel.

3.4.3 ELECTROCHEMICAL IMPEDANCE STUDIES

Nyquist plots for mild steel in 1N HCl containing different concentrations of inhibitors are shown in Figure 3.4.8 (a - e).Various impedance parameters such as charge transfer resistance (R_t) , double layer capacitance (C_{dl}), corrosion current density (I_{corr}) and inhibition efficiency (I E) calculated from these plots are given in Table 3.4.8.

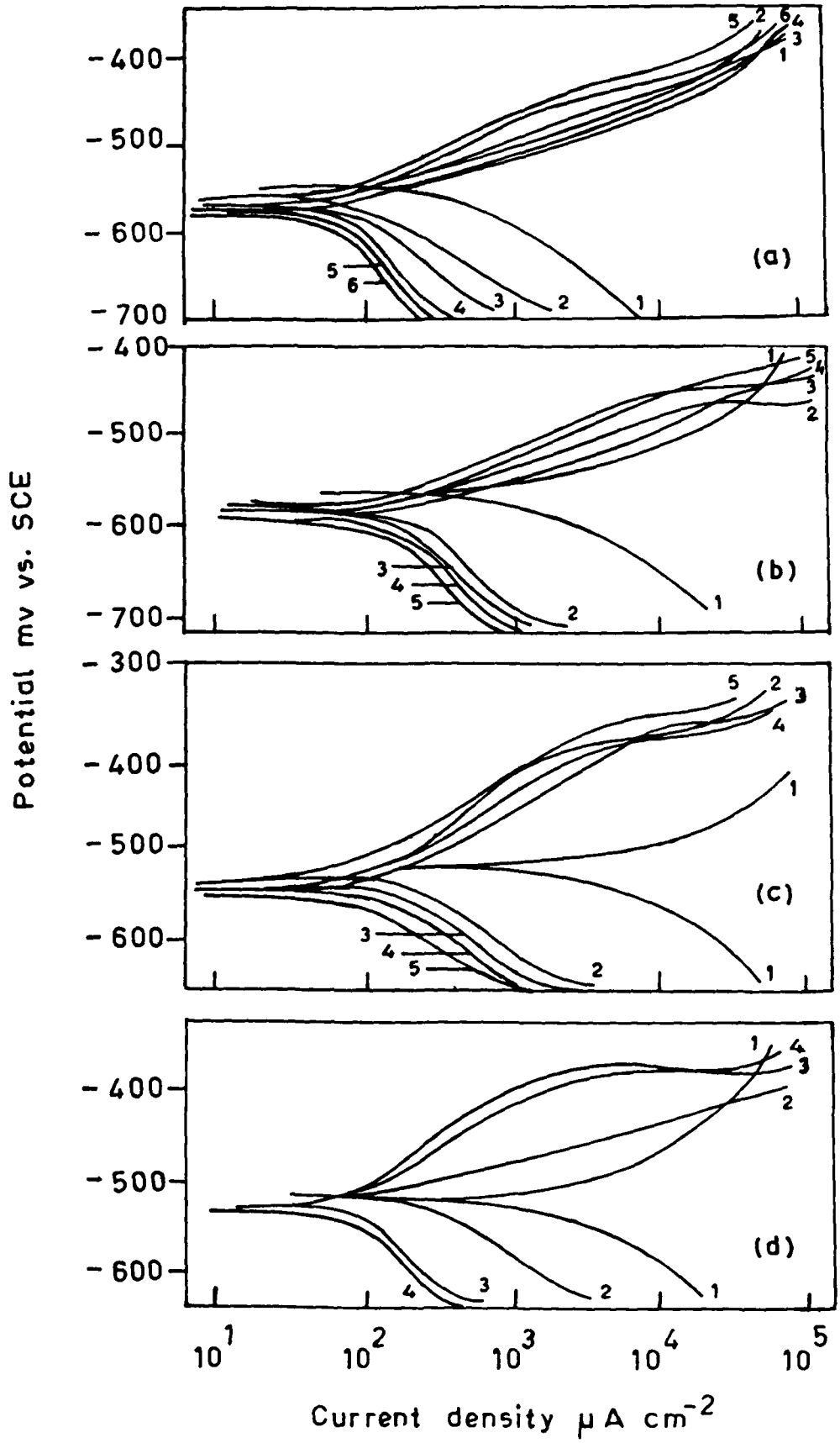


FIGURE 3.4.3 Potentiodynamic polarization curves for mild steel containing different concentrations of CTCH in : –

(a) 1N HCl : 1. Blank 2. 50 ppm 3. 100 ppm 4. 300 ppm 5. 400 ppm 6. 500 ppm
(b) 3N HCl : 1. Blank 2. 100 ppm 3. 300 ppm 4. 500 ppm 5. 700 ppm
(c) 5N HCl : 1. Blank 2. 300 ppm 3. 500 ppm 4. 700 ppm 5. 1000 ppm
(d) 5N HCl : 1. Blank 2. 5N HCl + KI 3. 300ppm + KI 4. 500 ppm + KI

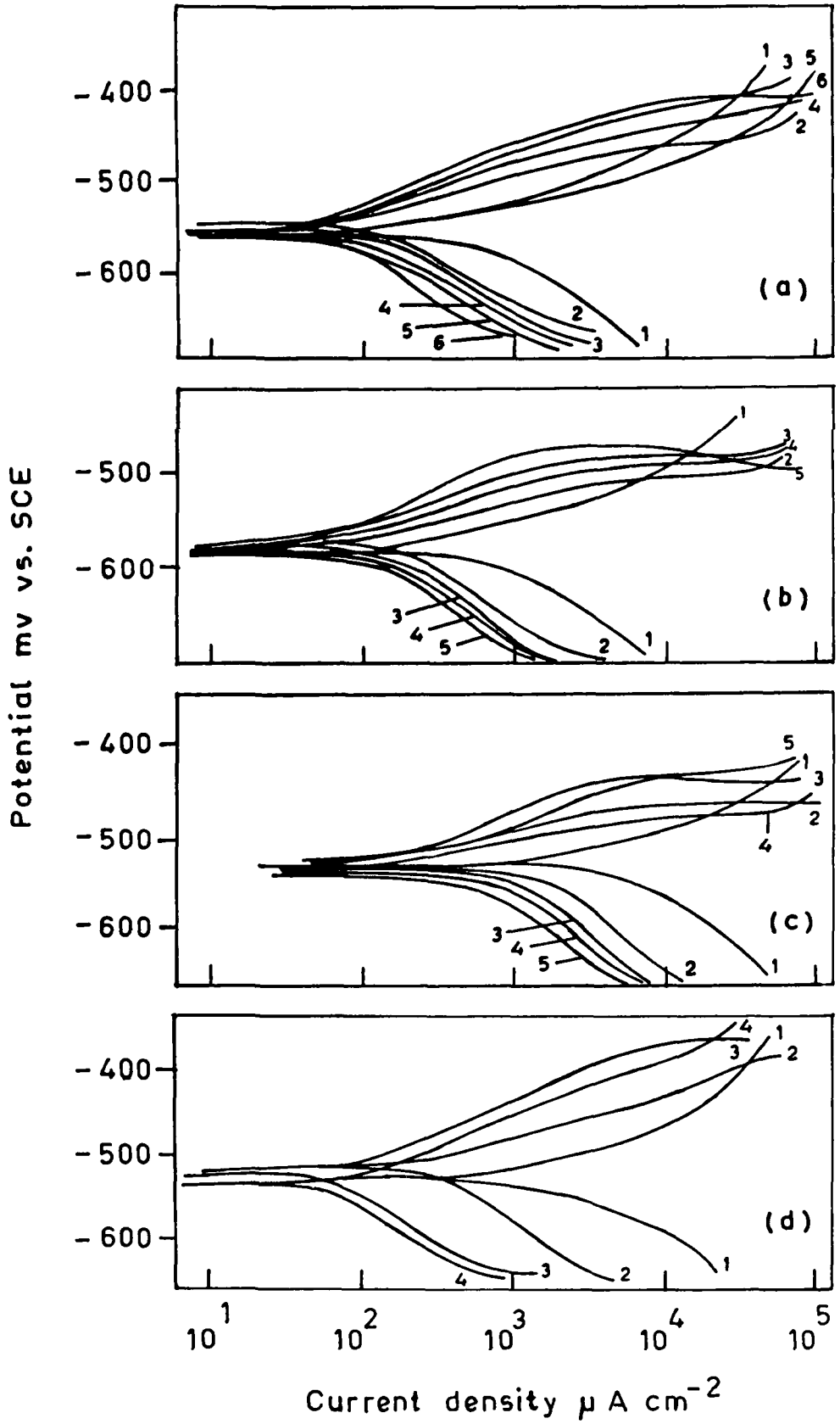


FIGURE 3.4.4 Potentiodynamic polarization curves for mild steel containing different concentrations of VTCH in : –

(a) 1N HCl : 1. Blank 2. 50 ppm 3. 100 ppm 4. 300 ppm 5. 400 ppm 6. 500 ppm
(b) 3N HCl : 1. Blank 2. 100 ppm 3. 300 ppm 4. 500 ppm 5. 700 ppm
(c) 5N HCl : 1. Blank 2. 300 ppm 3. 500 ppm 4. 700 ppm 5. 1000 ppm
(d) 5N HCl : 1. Blank 2. 5N HCl + KI 3. 300ppm + KI 4. 500 ppm + KI

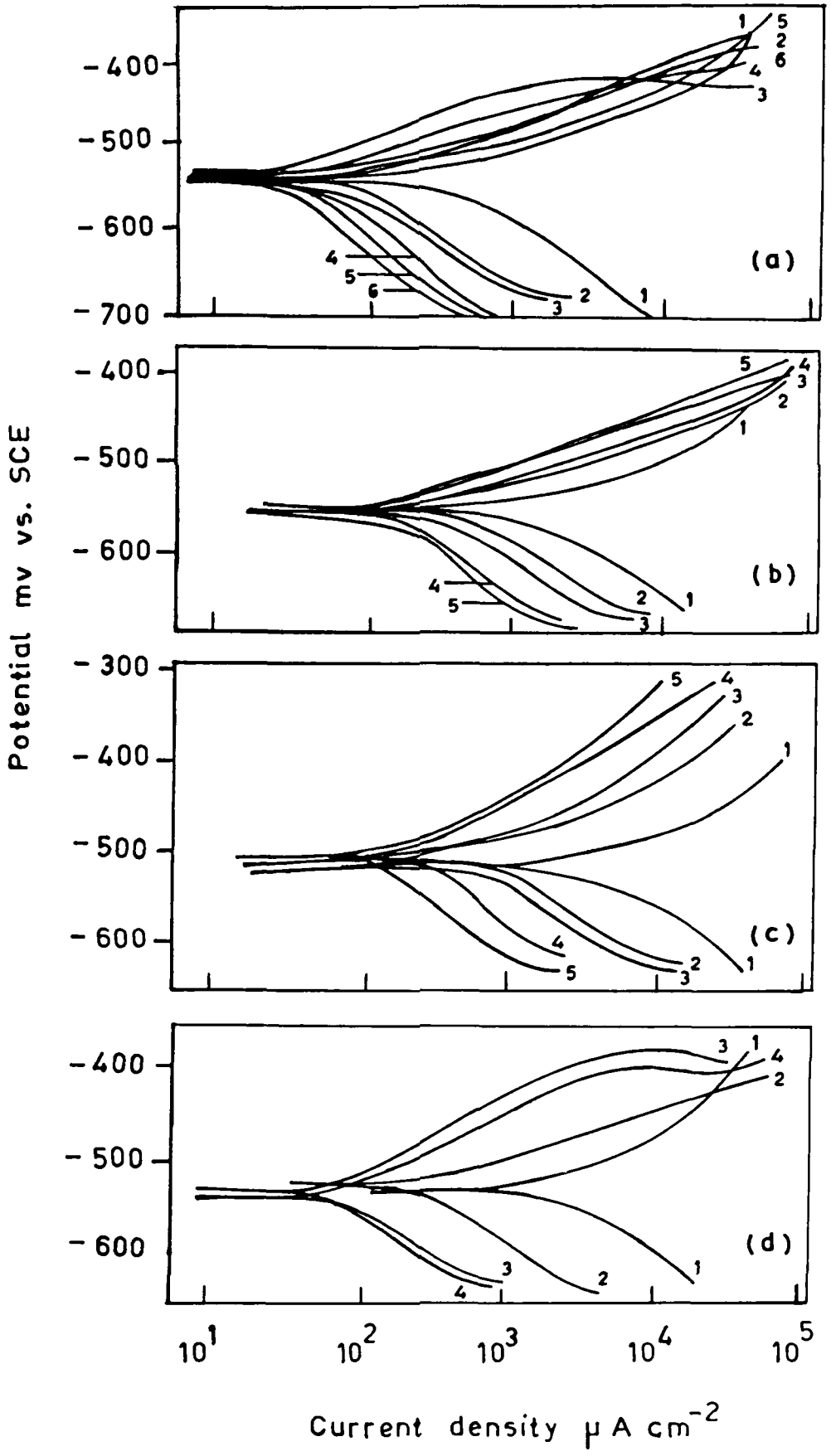


FIGURE 3.4.5 Potentiodynamic polarization curves for mild steel containing different concentrations of STCH in –

(a) 1N HCl	1	Blank	2	50 ppm	3	100 ppm	4	300 ppm	5	400 ppm	6	500 ppm
(b) 3N HCl	1	Blank	2	100 ppm	3	300 ppm	4	500 ppm	5	700 ppm		
(c) 5N HCl	1	Blank	2	300 ppm	3	500 ppm	4	700 ppm	5	1000 ppm		
(d) 5N HCl	1	Blank	2	5N HCl + KI	3	300ppm + KI	4	500 ppm + KI				

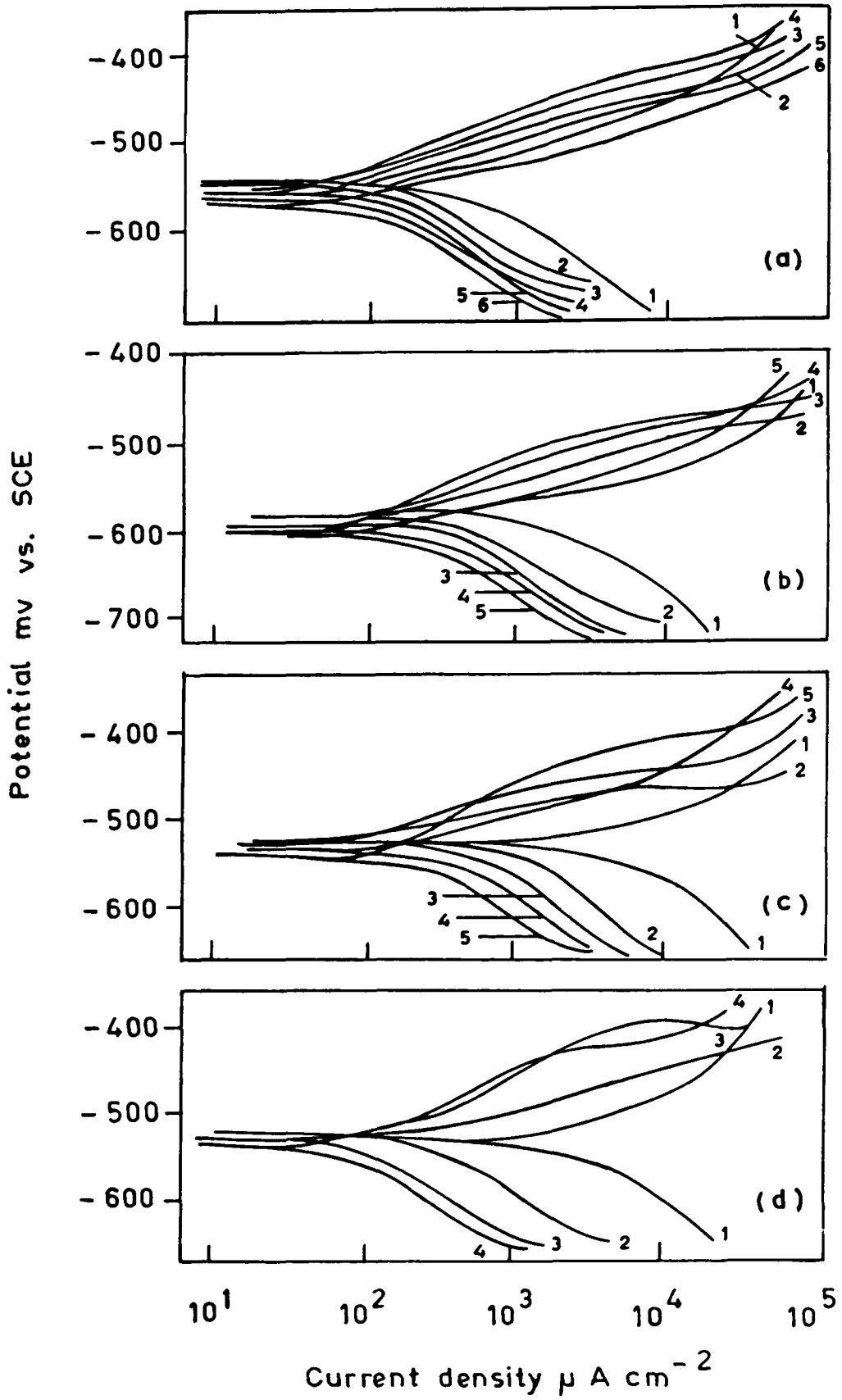


FIGURE 3.4.6 Potentiodynamic polarization curves for mild steel containing different concentrations of FTCH in : –

(a) 1N HCl :	1. Blank	2. 50 ppm	3. 100 ppm	4. 300 ppm	5. 400 ppm	6. 500 ppm
(b) 3N HCl :	1. Blank	2. 100 ppm	3. 300 ppm	4. 500 ppm	5. 700 ppm	
(c) 5N HCl :	1. Blank	2. 300 ppm	3. 500 ppm	4. 700 ppm	5. 1000 ppm	
(d) 5N HCl :	1. Blank	2. 5N HCl + KI	3. 300ppm + KI	4. 500 ppm + KI		

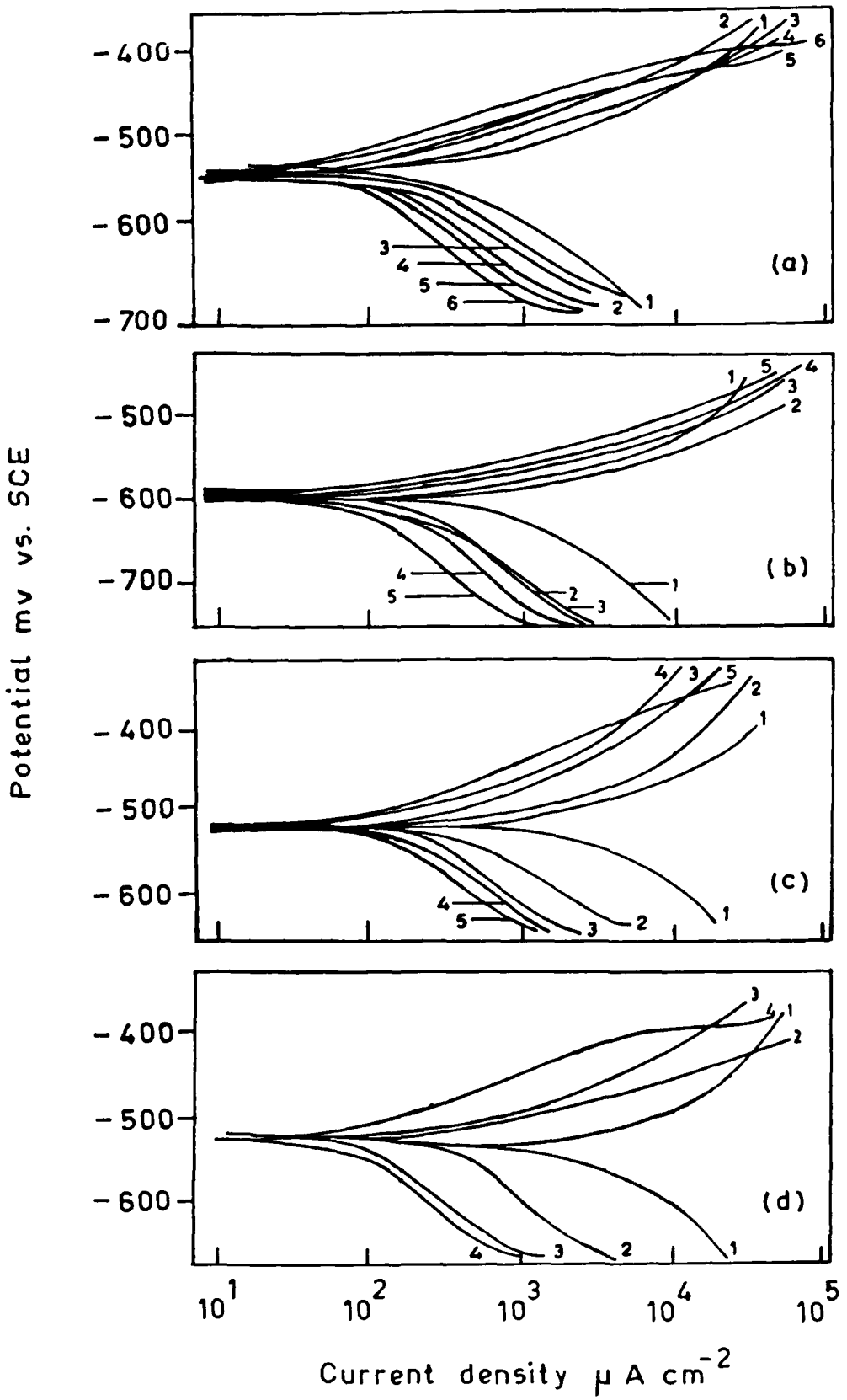


FIGURE 3.4.7 Potentiodynamic polarization curves for mild steel containing different concentrations of BTCH in : –

(a) 1N HCl : 1. Blank 2. 50 ppm 3. 100 ppm 4. 300 ppm 5. 400 ppm 6. 500 ppm
(b) 3N HCl : 1. Blank 2. 100 ppm 3. 300 ppm 4. 500 ppm 5. 700 ppm
(c) 5N HCl : 1. Blank 2. 300 ppm 3. 500 ppm 4. 700 ppm 5. 1000 ppm
(d) 5N HCl : 1. Blank 2. 5N HCl + KI 3. 300ppm + KI 4. 500 ppm + KI

Table 3.4.8 - Impedance data of mild steel in 1N HCl containing different concentrations of substituted thiocarbohydrazides.

SYSTEM	Inhi. Conc. (ppm)	R_t (Ω cm^2)	C_{dl} (μF cm^{-2})	I_{corr} (μ A cm^{-2})	I E (%)
1N HCl	–	115	12832	155	–
CTCH	300	2300	791	7.70	95.00
	500	2600	729	6.97	95.58
VTCH	300	1800	994	10.60	93.61
	500	2051	833	8.48	94.40
STCH	300	1630	1097	11.06	92.95
	500	1874	951	9.28	93.86
FTCH	300	1030	1452	19.68	88.84
	500	1118	1414	17.69	89.72
BTCH	300	907	2356	21.79	87.33
	500	1000	1511	17.39	88.50

It is seen that R_t values increase on increasing concentration of inhibitors, while C_{dl} and I_{corr} values decrease. Maximum increase in R_t value was observed in case of CTCH.These observations indicate that CTCH is the most effective corrosion inhibitor. It is found to decrease C_{dl} value from 12832 μ F cm^{-2} to 729 μ F cm^{-2}, suggesting that it inhibits corrosion by adsorption mechanism. All of the tested compounds follow the same order of inhibition efficiency as obtained by weight loss and electrochemical potentiodynamic polarization methods.

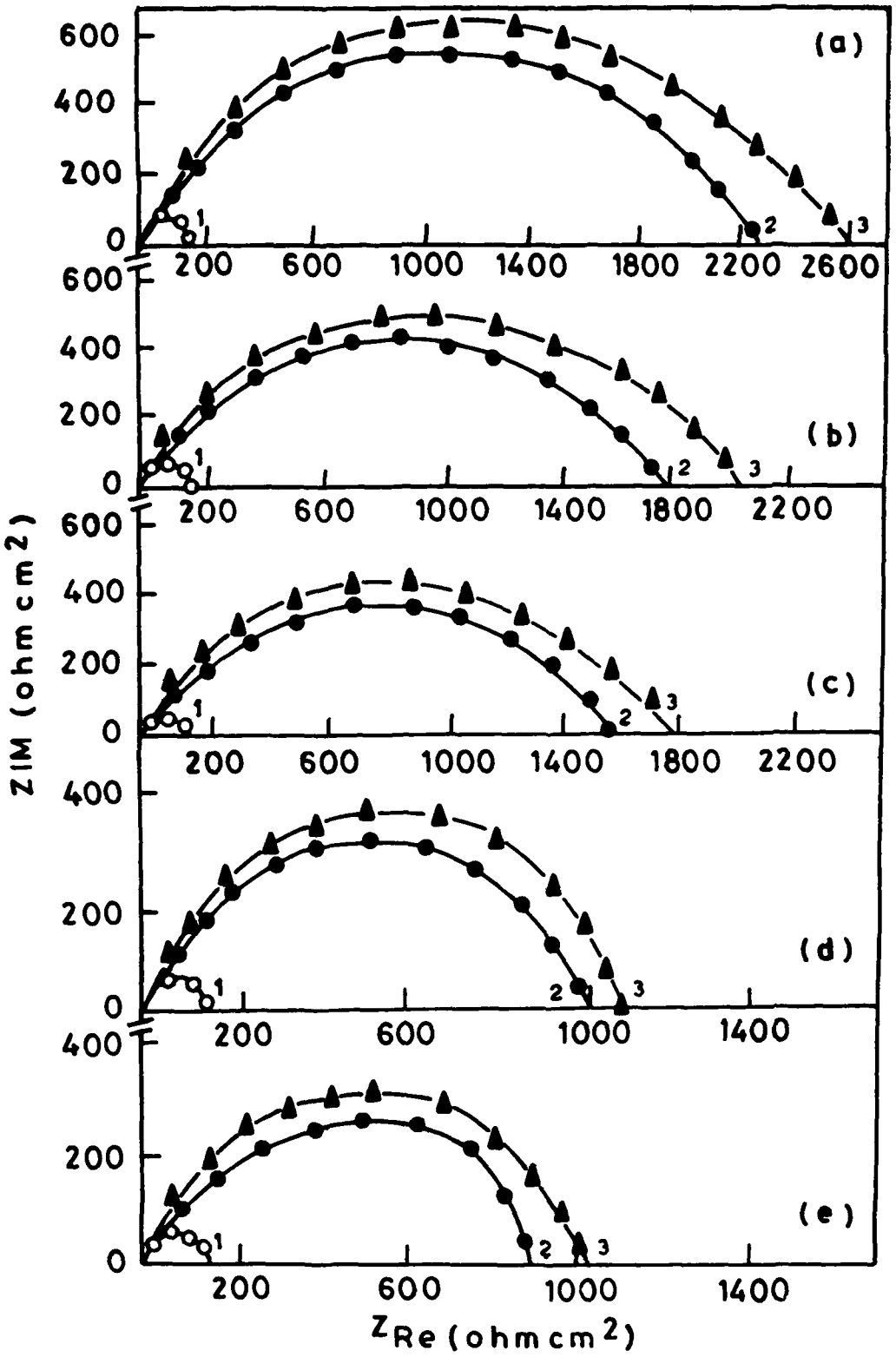


FIGURE 3.4.8 Nyquist plots for mild steel in 1N HCl *in absence and presence different* concentrations of substituted thiocarbohydrazides –
(a) CTCH (b) VTCH (c) STCH (d) FTCH (e) BTCH 1 Blank 2 300 ppm 3 500 ppm

3.4.4 HYDROGEN PERMEATION STUDIES

Hydrogen permeation current vs time curves for mild steel in 1N HCl in absence and presence of 500 ppm of BTCH and CTCH are shown in Figure 3.4.9. The values of permeation current and percent reduction for two inhibitors are given in Table 3.4.9. It is observed that both the compounds reduce the hydrogen permeation current in 1N HCl from 24 μA to 15 μA and 12μA respectively. The decrease in hydrogen permeation may be attributed to the adsorption of inhibitor molecule on the metal surface, which inhibited the entry of hydrogen into the metal.

Table 3.4.9 - Hydrogen permeation parameters for mild steel in 1N HCl containing 500 ppm of substituted thiocarbohydrazides at 35 ± 2°C.

Inhi. Conc. (ppm)	Permeation current (μ A)	Percent reduction (%)
1N HCl	24	--
500 BTCH	15	37.5
500 CTCH	12	54.1

3.4.5 AUGER ELECTRON SPECTROSCOPIC STUDIES

The auger electron spectrum for polished mild steel surface, steel exposed to a solution of CTCH and CTCH + KI in 1N HCl are shown in Figure 3.4.10 (a - c). The appearance of peaks at 152 and 378 ev confirms the adsorption of CTCH through S and N atoms, similarly appearance of peaks at 512, 378 and 152 ev proves the presence of iodine, nitrogen and sulphur atoms respectively on mild steel surface inhibited with CTCH in presence of KI.

The values of concentration of the different elements present in mild steel and on the adsorbed inhibitor film are given in Table 3.4.10. These data show the concentration of nitrogen, sulphur and iodine atoms in the adsorbed film of inhibitor.

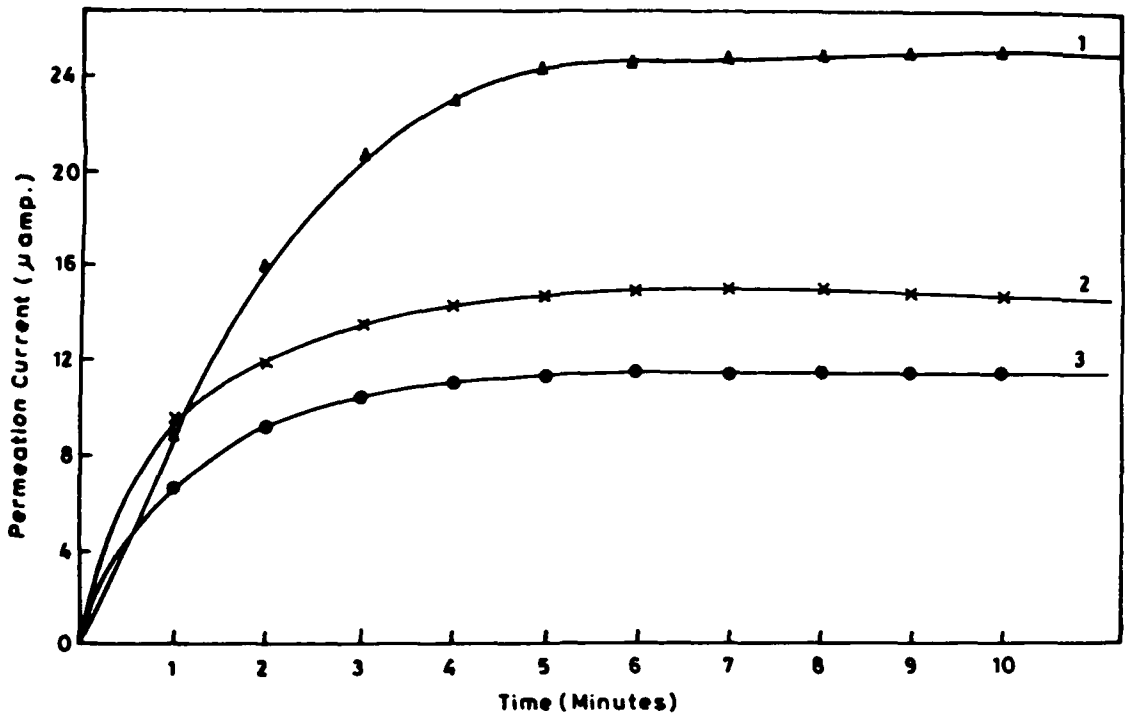


FIGURE 3.4.9 Hydrogen permeation curves for mild steel in 1N HCl in absence and presence of 500 ppm of substituted dithiobiurets :–

1. Blank 2. BTCH 3. CTCH

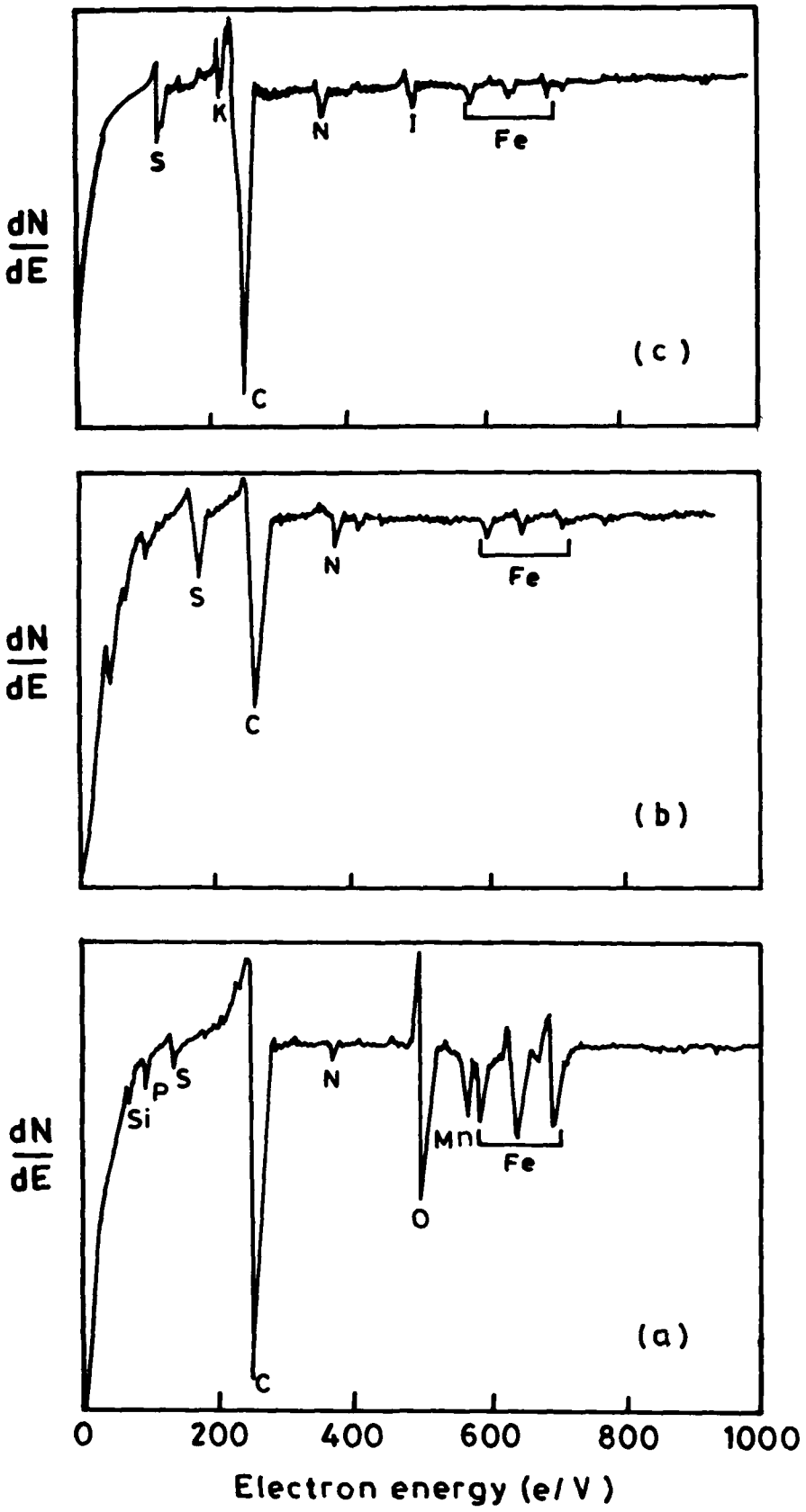


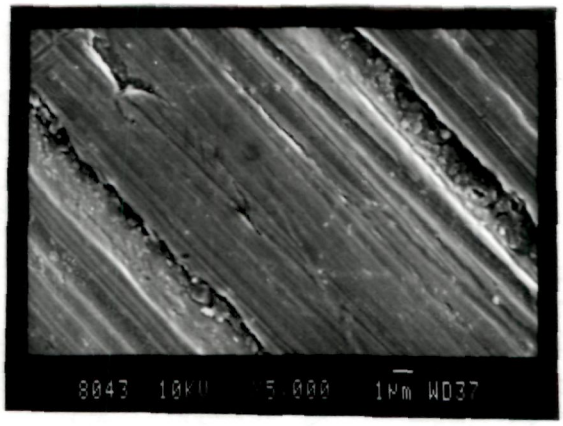
FIGURE 3.4.10 Auger electron spectrum for .–
(a) polished mild steel surface (b) mild steel exposed to CTCH
(c) mild steel exposed to CTCH + KI

Table 3.4.10 - Elemental composition of mild steel obtained from auger electron spectroscopy in presence of CTCH and CTCH + KI in 1N HCl.

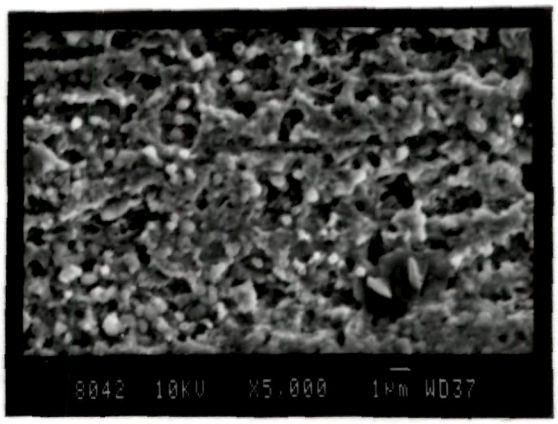
Element	Peak height (mm)	Relative senstivity (S_x)	Composition (%)
MILD STEEL			
C	122	0.20	57.50
O	73	0.50	13.80
P	10	0.50	1.81
S	9	0.80	1.06
N	4	0.32	1.18
Mn	22	0.23	9.02
Si	2	0.35	0.54
Fe	32	0.20	15.09
CTCH			
C	64	0.20	74.74
S	23	0.80	6.71
N	11	0.32	8.03
Fe	9	0.20	10.51
CTCH + KI			
C	115	0.20	78.96
S	22	0.80	3.77
N	11	0.32	4.72
Fe	8	0.20	5.49
K	16	0.80	2.74
I	10	0.32	4.00

3.4.6 SCANNING ELECTRON MICROSCOPIC STUDIES

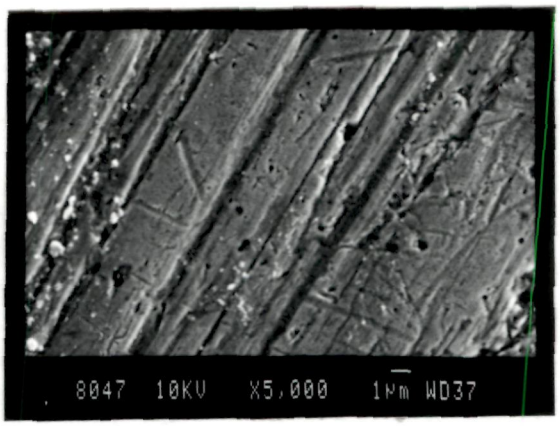
To ascertain the inhibition of corrosion of mild steel in 1N HCl by CTCH, SEM photographs of plain mild steel, steel exposed to 1N HCl and to a solution of 500 ppm CTCH in 1N HCl were taken. It is clear from these photographs [Figure 3.4.11 (a - c)] that surface of plain mild steel and steel exposed to 1N HCl containing 500 ppm CTCH are smooth as compared to mild steel exposed to 1N HCl. These observations indicate that CTCH inhibits the corrosion of mild steel by forming a adsorbed film on the mild steel surface.



(a)



(b)



(c)

FIGURE 3.4.11 Scanning electron micrographs for :–
(a) Polished mild steel (b) Mild steel in 1N HCl
(c) Mild steel in 1N HCl + 500 ppm CTCH

3.4.7 CONCLUSION

The main conclusions drawn from these studies are :—

1. All of the investigated substituted thiocarbohydrazides show good inhibition efficiency in the acid solutions (1 - 5N HCl). Their order of IE is : –

   CTCH > VTCH > STCH > FTCH > BTCH

2. Their inhibition efficiency increases with the increase in inhibitor concentration, temperature and immersion time whereas decreases with the increase in acid concentration.

3. IE of all the compounds increases on addition of KI due to synergism.

4. The adsorption of these compounds on the mild steel surface from all acidic solutions obeys Temkin's adsorption isotherm.

5. Potentiodynamic polarization study reveal that STCH, VTCH and BTCH behave as mixed inhibitors whereas CTCH and FTCH act as predominantly cathodic in 1 - 5N HCl solutions

6. EIS studies show that in the presence of all substituted thiocarbohydrazides R_t value increases while C_{dl} decreases in 1N HCl.

7. The investigated compounds namely CTCH and BTCH bring down hydrogen permeation current.

8. AES analysis substantiates the adsorption of CTCH on mild steel surface through N or S atoms and also supports the synergistic effect of KI on CTCH.

9. SEM micrographs of mild steel exposed to inhibitor solution show smooth surface of mild steel.

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SUMMARY

Corrosion is a major problem in several industries. It causes enormous economic wastage of metallic materials, which leads to heavy economic losses all over the world. In India the monetary losses due to corrosion have been estimated as high as Rs. 25,000 crores per year.

Among the available methods of preventing corrosion the use of inhibitors is one of the most promising methods, particularly for closed systems. Due to ease of application and cost effectiveness it has attracted a great deal of attention of corrosion scientists and engineers all over the world.

Mild steel is one of the most important engineering metal, which due to its low cost and excellent mechanical properties is widely used as a construction material. The mild steel is severely attacked in acid solutions, as it usually comes in contact with HCl and H_2SO_4 in various industries during pickling cleaning of industrial equipments and acidization of oil wells etc. Inhibited acid solutions are commonly used to reduce the corrosive attack of acid on metals. The use of inhibitors is specific for different systems and thus it needs to be studied thoroughly.

The research work described in the thesis deals with the study of nitrogen and sulphur containing organic compounds as corrosion inhibitors for mild steel in 1N, 3N and 5N HCl at 40°C. Some organic compounds have been evaluated in 1N HCl and 1N H_2SO_4 at room temperature. The molecular structures and names of these compounds are given in Table 1.0. The techniques such as weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy, hydrogen permeation, auger electron spectroscopy and scanning electron microscopy have been used in these studies on corrosion inhibition.

The thesis comprises of three chapters. The first chapter presents a general introduction which highlights the economic and technological importance of corrosion. Theories of corrosion have also been described, which help in understanding the mechanism of corrosion. Special attention has been given to explain the mode of action of inhibitors towards corrosion control. The account of various techniques used for investigating corrosion inhibitors have been discussed briefly. A survey of the literature on corrosion inhibitors for mild steel in acid solution has also been given.

The aims and objectives have also been mentioned.

The description of inhibitor synthesis and the details of experimental techniques such as weight loss, potentiodynamic polarization, AC impedance, hydrogen permeation, auger electron spectroscopy and scanning electron microscopy used in these studies are given in second chapter.

The third chapter describes the discussion of results obtained during these studies. The compounds of which inhibitive action has been studied are tabulated. Their inhibiting action have been discussed separately in following sections :-

(i) Macrocyclic compounds (ii) Substituted Thiobisformamidines

(iii) Substituted Dithiobiurets (iv) Substituted Thiocarbohydrazides

The results of these investigations revealed the fact that all of the macrocyclic compounds inhibit the mild steel corrosion effectively in acid solutions. The maximum value of inhibition efficiency is achieved at 500, 700 and 2000 ppm in 1N, 3N and 5N HCl at 40°C in the following order:-

PTAT > PTAB > POAB

The difference in inhibitive action of macrocyclic compounds has been explained in terms of the number and nature of heteroatoms, present in them. The effect of macrocyclic compounds studied in 1N HCl and H_2SO_4 at room temperature (35± 2°C) exhibited inhibition efficiency in the following order:-

TBOAD > DBOAD > BMOAT > BOAH > MOAT >OAH

The difference in inhibition efficiency of these compounds can be explained on the basis of the number of aromatic rings present in them. TBOAD contains four aromatic rings and so it has exhibited highest inhibition efficiency, whereas OAH showed lowest inhibition efficiency due to the absence of aromatic ring in it.

The inhibition efficiencies of substituted thiobisformamidines in 1N, 3N and 5N HCl follow the order:-

CPTBF > ATBF > TTBF > PTBF

Among these four compounds chloro derivative showed highest inhibition efficiency due to its high dipole moment than other compounds. The better performance of ATBF than TTBF has been explained on the basis of Pearson's hard and soft acid

base principle (HSAB). The order of inhibition efficiency of different dithiobiurets has been found to be as follows:-

APDTB > TPDTB > DPDTB >CPDTB

The better performance of APDTB may be attributed to the presence of electron releasing $-OCH_3$ group. The lowest value of inhibition efficiency for CPDTB among the studied compounds can be explained on the basis of – I effect (electron withdrawing inductive effect) of chloro group on the reaction site thus showing less adsorption and less inhibition of corrosion. The inhibition efficiency values of substituted thiocarbohydrazides in 1N, 3N and 5N HCl solutions follow the order:-

CTCH > VTCH > STCH > FTCH > BTCH

CTCH exhibited highest inhibition efficiency among the studied thiocarbohydrazides which can be explained due to the presence of an additional π bond between carbon atoms –C = C conjugated to azomethine group (–C = N) . VTCH shows better inhibition efficiency than STCH due to the presence of an additional electron releasing methoxy group (– OCH_3). STCH is found to exhibit superior inhibition efficiency than FTCH due to presence of –OH group. The better performance of FTCH than BTCH may be attributed to the presence of lone pairs of electrons on oxygen atom through which it can adsorb more strongly than BTCH leading to high inhibition efficiency.

The effect of temperature, immersion period and inhibitor concentration has also been studied on inhibition efficiency of all the investigated compounds. The following conclusions have been drawn:-

1. Inhibition efficiency of Thiocarbohydrazides, Thiobisformamidines and Dithiobiurets increases on increasing the temperature from 40-70°C, whereas the inhibition efficiency of macrocyclic compounds decreases on rise in temperature.
2. The inhibition efficiency of all the compounds increases on increasing the immersion period (24 - 96 hours) as well as inhibitor concentration.
3. The inhibition efficiency of these compounds decreases on increasing the acid concentration from 1N - 5N.

An interesting feature of these investigations is that inhibition efficiency of all the tested compounds increased on the addition of small amount of KI to acid solutions due to synergism. The synergistic effect has also been found to be more pronounced in case of substituted dithiobiurets.

Sixteen compounds out of twenty two were evaluated as corrosion inhibitors in 5N HCl in 70°C. The compound CTCH has given highest inhibition efficiency of 99% among the tested compound at a concentration of 500 ppm in 5N HCl at 70°C.

Potentiodynamic polarization studies reveal that all the tested inhibitors are mixed inhibitors except CTCH, FTCH, TPDTB and CPDTB, which showed predominantly cathodic behavior in 1- 5N HCl. The compounds BMOAT, MOAT, BOAH and OAH exhibited mixed nature in 1N HCl and predominantly cathodic behavior in 1N H_2SO_4.

Selected compounds were evaluated through electrochemical impedance spectroscopic technique in 1N HCl solution. CTCH has been found to be more effective inhibitor as it increased the R_t value more than other compounds.

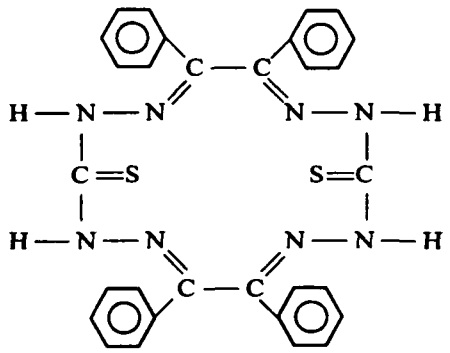
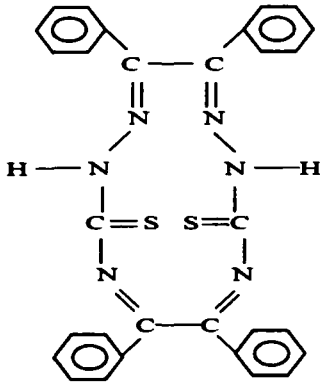
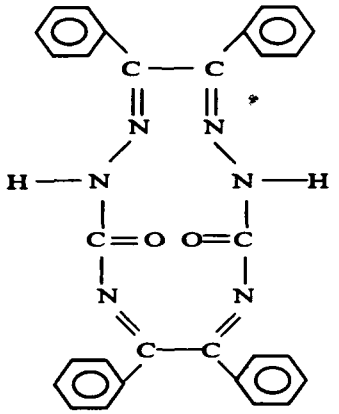
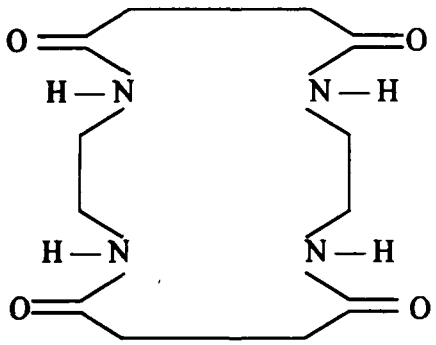
The compounds selected for hydrogen permeation tests were found to reduce the hydrogen permeation current in 1N HCl. Maximum reduction in hydrogen permeation current was observed in case of CTCH and minimum in case of PTAB.

The order of inhibitive performance of various classes of organic compounds examined in the present investigations is :-

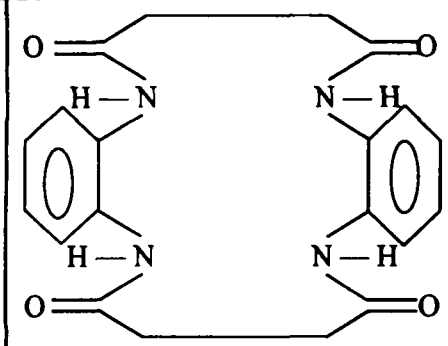
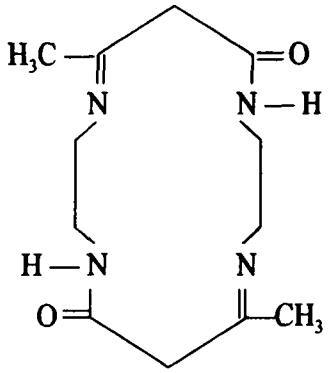
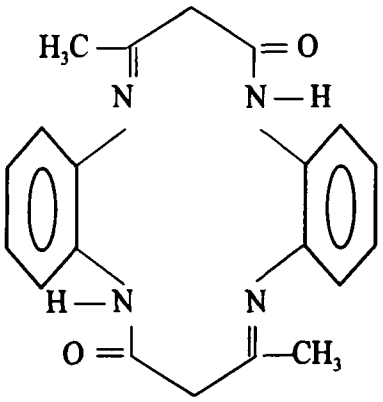
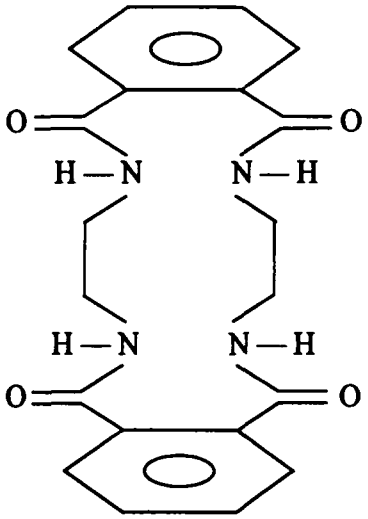
Dithiobiurets > Thiocarbohydrazides > Thiobisformamidines > Macrocyclic compounds

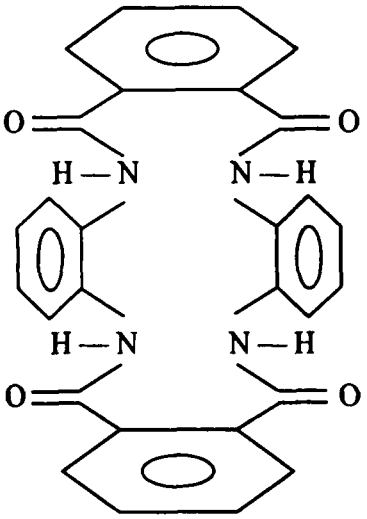
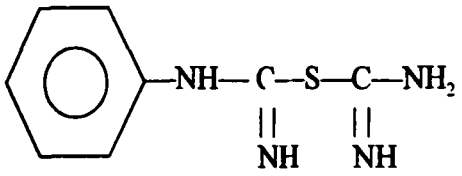
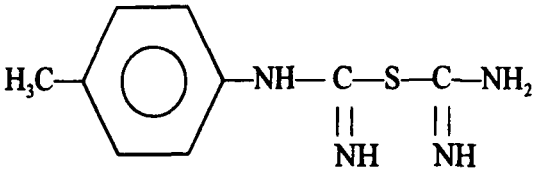
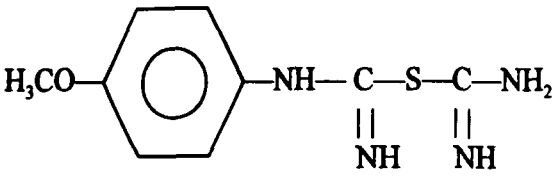
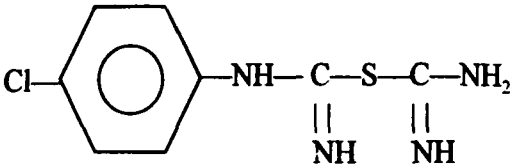
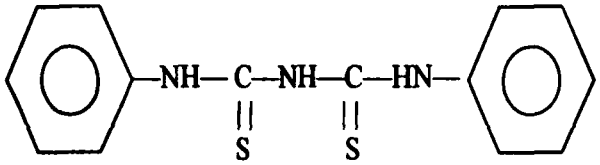
The results of auger electron spectroscopy (AES) studies show that the adsorption of inhibitor molecules on the metal surface occurs through heteroatoms such as N, S or O atoms. The better appearance of mild steel surface in inhibited acid solution than in plain acid solutions as evident from scanning electron microscopic (SEM) studies further supports the fact that inhibitor molecules are adsorbed over the steel surface and prevent the attack of corrosive acid solutions on the steel surface.

TABLE 1.0:- NAME AND STRUCTURAL FORMULAE OF THE INHIBITORS USED

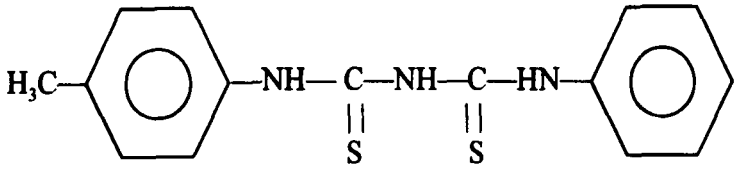
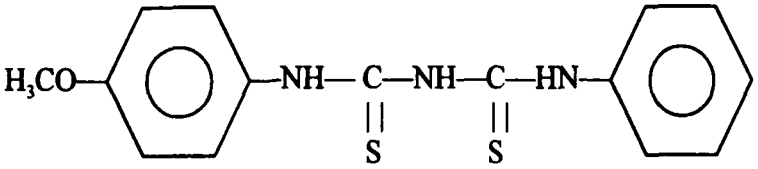
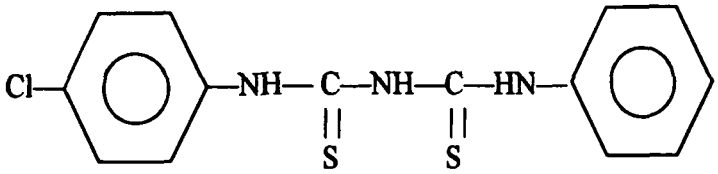
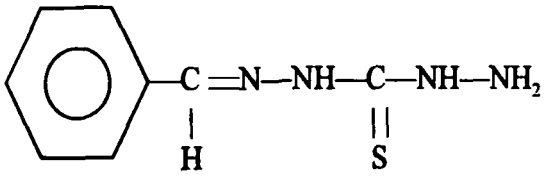
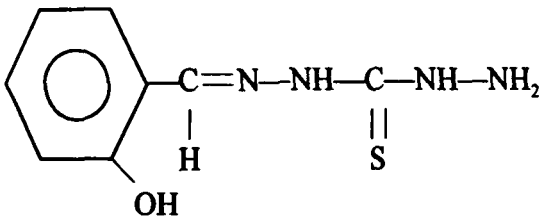
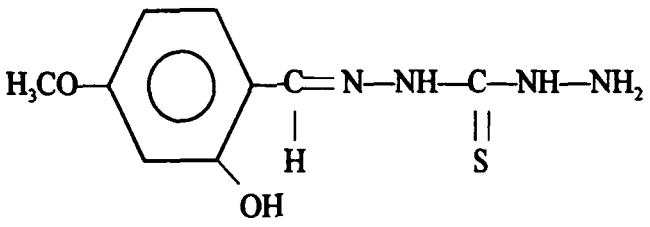
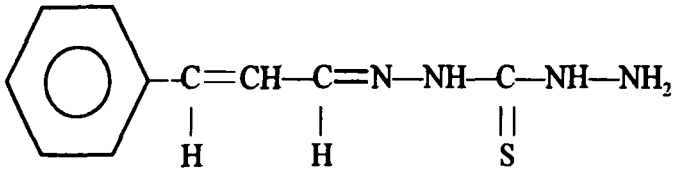
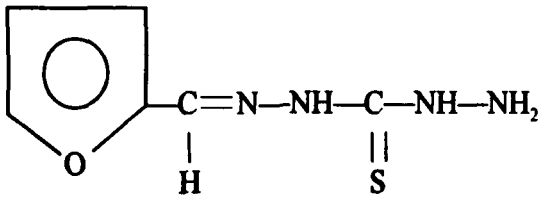
S.No.	STRUCTURAL FORMULA	DESIGNATION AND ABBRIVIATION
1		Tetraphenyl-dithia-octaaza-cyclotetradecane hexaene (PTAT)
2		Tetraphenyl-dithia-hexaaza-cyclobidecane hexaene (PTAB)
3		Tetraphenyl-dioxo-hexaaza-cyclobidecane hexaene (POAB)
4		2,5,10,13-tetraoxo-1,6,9,14-tetraazacyclohexadecane (OAH)

Contd —

S.No.	STRUCTURAL FORMULA	D ESIGNATION AND ABBRIVIATION
5		7,8:15,16-dibenzo-2,5,10,13-tetraoxo-1,6,9,14 -tetraazacyclo-hexadecane (BOAH)
6		7,14-dimethyl-5,12-dioxo-1,4,8,11-tetaazacyclotetradeca-1,7-diene (MOAT)
7		2,3:9,10-dibenzo-7,14-dimethyl-5,12-dioxo-1,4,8,11-tetraaza-cyclotetradeca-1,7-diene (BMOAT)
8		3,4:11,12-dibenzo 2,5,10,13-tetraoxo-1,6,9,14-tetraazacy-clohexadecane (DBOAD)

S.No.	STRUCTURAL FORMULA	DESIGNATION AND ABBRIVIATION
9		3,4:7,8:11,12:15,16-tetrabenzo-2,5,10,13-tetraoxo-1,6,9,14-tetraazacyclohexadecane (TBOAD)
10		Phenyl Thiobisformamidine (PTBF)
11		Tolyl Thiobisformamidine (TTBF)
12		Anisidyl Thiobisformamidine (ATBF)
13		4-cholrophenyl Thiobisformamidine (CPTBF)
14		1,5-diphenyl-2,4-dithiobiuret (DPDTB)

Contd ---

S.No.	STRUCTURAL FORMULA	DESIGNATION AND ABBRIVIATION
15		1-tolyl-5-phenyl- 2,4 -dithiobiuret (TPDTB)
16		1-anisidyl-5-phenyl-2,4-dithiobiuret (APDTB)
17		1-chlorophenyl-5-phenyl-2,4 dithiobiuret (CPDTB)
18		1-benzylidene-3-thiocarbohydrazide (BTCH)
19		1-salicylidene-3-thiocarbohydrazide (STCH)
20		1-vanillidene-3-thiocarbohydrazide (VTCH)
21		1-cinnamylidene-3-thiocarbohydrazide (CTCH)
22		1-furfurylidene-3-thiocarbohydrazide (FTCH)

LIST OF PUBLICATIONS

1. Corrosion inhibiting properties of some polyaza macrocyclic compounds on mild steel in acid environments.
   Anti - Corrosion Methods and Materials (UK) 45, 6 (1998) 419-425

2. Macrocyclic compound as corrosion inhibitors
   (In press) Corrosion (USA)

3. Influence of some polyamide macrocyclic compounds on the inhibition of corrosion of mild steel in acidic solutions.
   (Accepted) Bulletin of Electrochemistry (India)

4. Tetramethyl - dithia - octaazacyclotetradecane - hexaene (MTAT) - A novel acid corrosion Inhibitor
   (Accepted) Anti - Corrosion Methods and Materials (UK)

5. Effect of some condensation products of glyoxal and diamines on mild steel corrosion in acid environments.
   (Communicated) The Electrochemical Society of India

6. Tetramethyl - dithia - hexaazacyclobidecane - hexaene (MTAT) - A novel acid corrosion Inhibitor
   (Communicated) Bulletin of Electrochemistry (India)

7. Thioamidine : A Novel class of acid Corrosion Inhibitors
   (Communicated) British corrosion Journal (London)

Contributed papers

Corrosion inhibiting properties of some polyaza macrocyclic compounds on mild steel in acid environments

Mohammad Ajmal
Jaya Rawat and
M.A. Quraishi

The authors

Mohammed Ajmal, Jaya Rawat and **M.A. Quraishi** work at the Corrosion Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh, Uttar Pradesh, India.

Abstract

Macrocyclic compounds constitute a potential class of corrosion inhibitors. In an attempt to develop effective corrosion inhibitors we have synthesized four macrocyclic compounds by condensing o-ethylene diamine and o-phenylene diamine with ethylacetoacetate and succinic acid. Their inhibiting action was evaluated on corrosion of mild steel in HCl and H_2SO_4 by weight loss and potentiodynamic polarization methods. A Macrocyclic compound derived by condensing o-phenylene diamine with ethylacetoacetate exhibited best performance by giving IE of 98 percent at 500ppm concentration. The potentiodynamic polarization studies revealed that the tested compounds are either mixed type or predominantly cathodic inhibitors. IE of all the investigated compounds increased significantly on addition of a small concentration KI in both acids due to synergism.

Introduction

The study of organic compounds as corrosion inhibitors has both scientific and technological significance. Corrosion scientists and engineers have shown a great deal of interest in the study of macrocylic compounds as corrosion inhibitors in recent years owing to their significant corrosion inhibiting properties for industrial metals and alloys [1,2]. In previous studies we have synthesized a few schiffs bases or anils by condensing an amine and a carbonyl compounds and evaluated their inhibiting action towards corrosion of mild steel in acidic solutions. The inhibition efficiency for all these compound have been found to be greater than those for corresponding amines [3,4]. In present investigations we have synthesized four macrocyclic compounds, namely: 2,3: 9, 10 - dibenzo- 7, 14-dimethyl-5, 12-dioxo-1,4,8, 11-tetraazacyclotetradeca- 1, 7-diene (BMOAT), 7, 14-dimethyl-5, 12-dioxo- 1, 4, 8, 11 -tetraazacyclotetradeca- 1, 7-diene (MOAT), 7, 8:15, 16- dibenzo-2,5, 1 O, 13-tetraoxo- 1,6,9, 14-tetraazacyclohexadecane (BOAH), 2, 5, 10, 13-tetraoxo-1, 6, 9, 14-tetraazacyclohexadecane (OAH) to study their inhibiting action on corrosion of mild steel in acid media.

Experimental procedures

Mild steel strips having size 2cm × 2cm × 0.025cm (C = 0.14 percent, Min = 0.35 percent, Si = 0.017, S = 0.25 percent, P = 0.03 percent and the rest being iron) were used for weight loss measurements. For potentiodynamic polarization studies, mild steel strips of the same composition coated with lacquer with an exposed area of $1cm^2$ were used. MS strips were polished with emery papers of 1/0, 2/0, 3/0, and 4/0 grade and degreased with trichloroethylene. AR grade HCl (MERCK) was used for preparing solutions. Double distilled water was used to prepare solutions of 1NHCl and 1N H_2SO_4 for all experiments. Weight loss studies were done using the ASTM standards[5].

Potentiodynamic polarization studies were carried out using the EG & G, PARC model 173, potentiostat/galvanostat universal programmer, model 175 and with x-y recorder,

One of the authors (J.R.) acknowledges the Council of Science and Technology U.P. Lucknow for the award of research fellowship.

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209

model RE 0089. A platinum foil was used as the auxiliary electrode, a saturated calomel electrode was used as the reference electrode and mild steel specimen as working electrodes for potentiodynamic polarization studies.

Macrocyclic compounds were synthesized in the laboratory following procedures as described in literature[6] and characterized by spectral data. Molecular structure and other details of the inhibitors used in the present studies are given in Table I.

Results and discussion

Weight loss experiments were carried out in 1 N HCl and 1 N H_2SO_4 at different concentrations, temperatures and immersion time. The results given in Table II show that IE increases with the increase in inhibitor concentration for all of the compounds and reaches maximum at an optimum concentration of 1,000ppm in both acids. The effect of inhibitor concentration on IE in HCl and H_2SO_4 has also been illstrated in Figure 1 (b and e).

The better performance of the BMOAT and BOAH as corrosion inhibitor than that of MOAT and OAH may be attributed to the presence of aromatic rings containing π electrons, which facilitate greater adsorption of BMOAT and BOAH on the metal surface. On the other hand, MOAT and OAH show lesser inhibition efficiency due to the lack of aromatic rings in these compounds. Desai *et al.* [7] have also reported that the condensation products derived from aromatic amines and carbonyl compounds give better inhibition efficiency than those derived from ethylene diamine and carbonyls.

Figures 1 (a and d) show the variation of IE with temperature. In both the acids, it is found that IE decreases with the increase in temperature. This indicates the fact that the inhibitor film formed on the metal surface is less protective in nature at high temperature. The desorption of the inhibitor molecules from the metal surface occurs at a faster rate at high temperature[8].

The variation of inhibition efficiency with immersion time in both acids has been shown in Figure 1 (c and f). The IE increases with the increase in immersion time. The increase in IE with increasing immersion time may be attributed to the formation of a barrier film which prevents the attack of acid on metal surface.

The better inhibition efficiency observed in 1N HCl than that of lN H_2SO_4 may be explained by the fact that chloride ions being less hydrated than sulphate ions are preferentially adsorbed on the metal surface, thereby creating an excess negative charge towards the solution phase which favours synergistic adsorption of protonated inhibitors on the metal surface [9, 10].

The values of IE for specific concentrations of inhibitors in combination with KI given in Table III show that IE increases with the addition of iodide ions for all of the compounds in the range of 10-40 percent. The similar synergistic effect has been reported by Quraishi *et al.* [11, 12]. The results obtained from potentiodynamic studies Table IV and V also substantiate the synergistic behaviour of macrocyclic compounds in presence of KI.

Adsorption isotherm

The plots of surface coverage θ V_s log C give a straight line in both acid solutions Figure 2(a and b), and show that the adsorption of macrocyalic compounds on mild steel/acidic solution interface obeys Temkin's adsorption isotherm.

Table I Structures of macrocyclic compounds

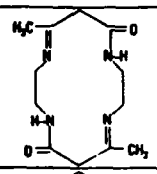
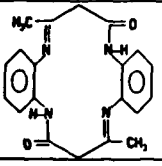
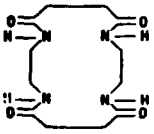
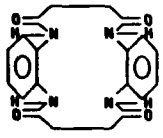
S. No.	STRUCTURAL FORMULA	DESIGNATION AND ABBREVIATION
1		7,14–dimethyl–5,12–dioxo–1,4,8, 11–tetraazacyclotetradeca–1,7–diene (MOAT)
2		2,3:9,10–dibenzo–7,14–dimethyl –5,12–dioxo–1,4,8,11–tetraaza– cyclotetradeca–1,7–diene (BMOAT)
3		2,5,10,13–tetraoxo–1,6,9,14– tetraazacyclohexadecane (OAH)
4		7,8:15,16–dibenzo–2,5,10,13– tetraoxo–1,6,9,14–tetraazacyclo– hexadecane (BOAH)

Table II Corrosion parameters obtained from weight loss studies in 1N HCl and 1N H_2SO_4 containing different concentration of macrocyclic compounds at 40°C for three hours

Inhibitor concentration (ppm)	1 N HCl I.E. (percent)	1 N HCl C.R. (mmpy)	1 N H_2SO_4 I.E. (percent)	1 N H_2SO_4 C.R. (mmpy)
No inhibitor	–	12.39	–	19.13
B MOAT				
100	64.4	4.41	30.5	13.28
200	77.5	2.78	37.1	11.23
300	82.7	2.13	40.2	11.82
400	85.0	1.85	50.0	9.40
500	90.2	1.20	51.4	9.13
1000	98.5	0.18	65.2	6.52
MOAT				
100	48.1	7.19	20.3	15.23
200	62.9	4.59	28.3	13.69
300	64.7	4.36	31.1	13.14
400	68.1	3.94	40.5	11.37
500	71.9	3.48	42.4	11.00
1000	84.6	1.90	54.1	8.77
BOAH				
100	56.1	5.43	23.0	14.72
200	66.2	4.17	32.7	12.64
300	70.7	3.62	35.9	12.25
400	74.1	3.20	41.2	11.23
500	74.9	3.05	46.3	10.26
1000	88.0	1.46	59.7	7.70
OAH				
100	47.5	6.50	10.9	17.04
200	53.1	5.80	18.6	15.55
300	63.3	4.55	21.1	15.09
400	68.5	3.90	25.2	14.30
500	68.9	3.85	27.1	13.93
1000	83.5	2.04	31.3	13.14

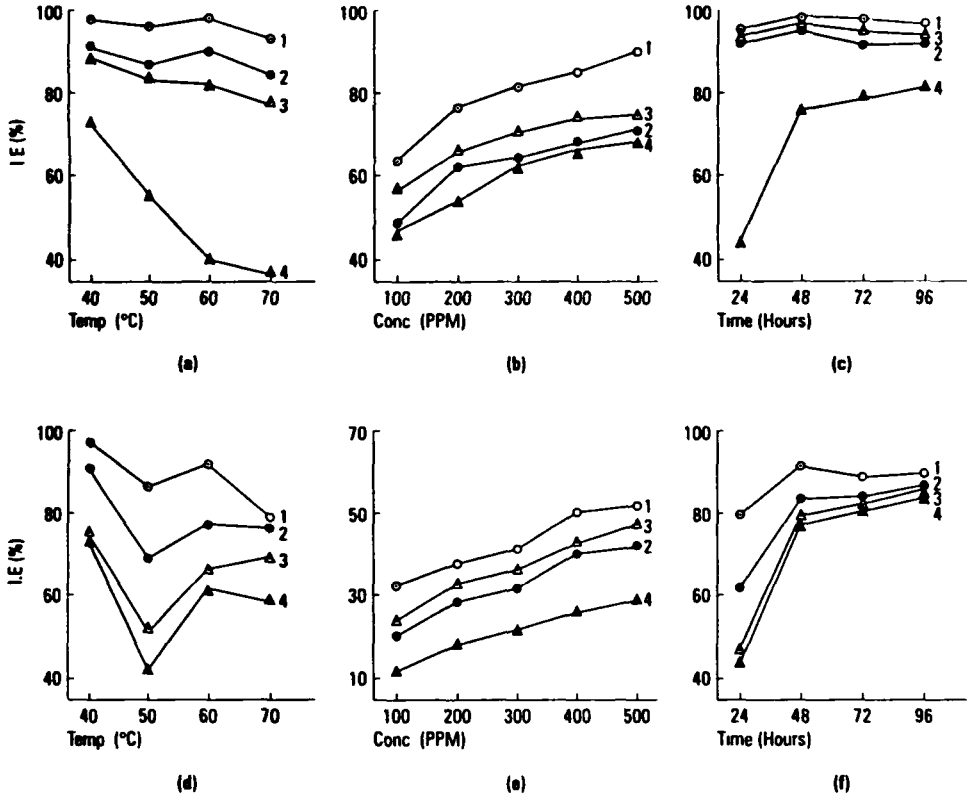
Potentiodynamic polarization studies

The cathodic and anodic polarization behaviour of mild steel in 1N HCl and 1N H_2SO_4 in absence and presence of optimum concentration of each inhibitor are shown in Figure 3 (a and b). Tables IV and V give values of corrosion current (I_{corr}), corrosion potential (E_{corr}), cathodic and anodic Tafel slopes b_c and b_a for all inhibitors in 1N HCl and 1N H_2SO_4 respectively. It can be seen that all these compounds give significantly lower I_{corr} values and maximum decrease in I_{corr} values at 1,000 ppm of each inhibitor in both acids. These results reveal that macrocyclic compounds do not shift E_{corr} values in 1N HCl but bring about slight shift of E_{corr} values in 1N H_2SO_4 towards negative side. These observations indicate that they are mixed type inhibitors in HCl and predominantly cathodic in H_2SO_4. The Tafel slope values do not change significantly in acidic sotutions in presence of these compounds. suggesting that these compounds inhibit the corrosion of mild steel by blocking the active sites of steel surface[12].

Mechanism of corrosion inhibition

The plausible mechanism of corrosion inhibition of mild steel in 1N HCl and 1N H_2SO_4 may be explained on the basis of adsorption. In acid solutions macrocyclic compounds exist as protonated species, which can adsorb on the cathodic sites of mild steel and decrease the evolution of hydrogen. The adsorption of these compounds on anodic

Figure 1 Variation of IE with temperature in 1N HCl (a), 1N H_2SO_4 (d), inhibitor concentration in 1N HCl (b), 1N H_2SO_4 (e), immersion time in 1N HCl (c), 1N H_2SO_4 (f) 1 BMOAT, 2 MOAT, 3 BOAH, 4 OAH



sites through lone pairs of electrons of nitrogen and π electrons of benzene ring may decrease anodic dissolution of mild steel.

Conclusions

- All of the macrocyclic compounds were found to inhibit the corrosion of mild steel in both acids.
- BMOAT and BOAH gave the better performance than MOAT and OAH in both acids
- All of these compounds performed well in both acids, even for long duration immersion tests conducted for 96 hours.
- Adsorption of these compounds on the mild steel surface from both acids was

Table III Inhibition efficiencies obtained from weight loss studies in absence and presence of KI with different concentration of macrocyclic compounds in 1N HCl and 1N H_2SO_4 at 40°C for three hours

Inhibitor concentration (ppm)	KI concentration (percent)	BMOAT	MOAT	BOAH	OAH
1N HCl					
300	-	82.77	64.79	70 78	63 30
300	0.02	97.38	95 88	97 75	70 64
400	-	85 02	68 16	74 16	68.54
400	0.02	98.88	98.50	99 25	77.52
1 N H_2SO_4					
400	-	50 00	40 53	41.26	25.24
400	0.03	98.30	83 90	96.36	78.88
500	-	51 46	42 48	46.36	27.18
500	0.03	99 27	87.86	98 54	91.75

2/2

Table IV Electrochemical polarisation parameters of mild steel in 1 N HCl in presence of different concentrations of macrocyclic compounds with and without KI at 35±2°C

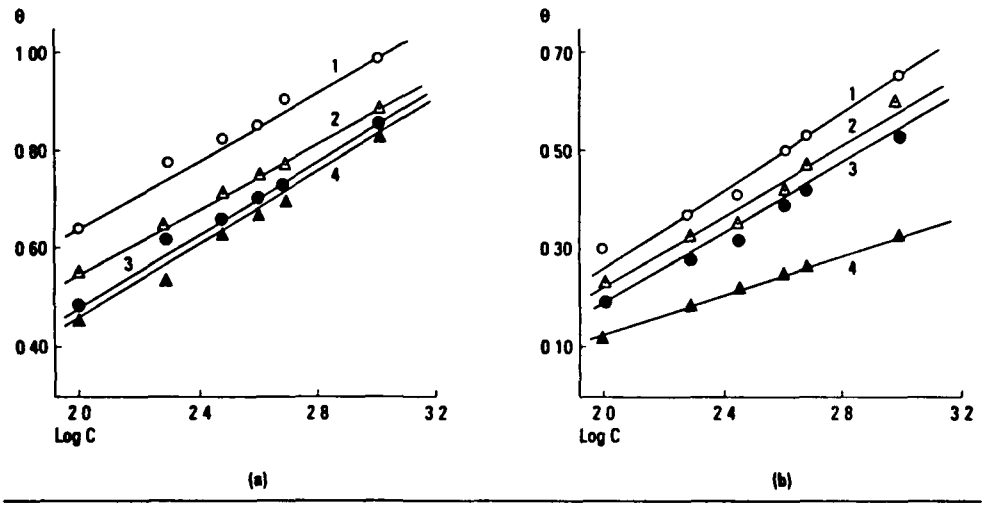
Inhibitor concentration (ppm)	E_{corr} (mv)	I_{corr} μAcm^{-2}	b_c $mvdec^{-1}$	b_a $mvdec^{-1}$	I.E. (percent)
No inhibitor	–554	350	130	60	–
B MOAT					
100	–546	180	120	50	48.57
400	–532	130	125	55	62.86
1000	–526	74	120	50	78.86
400 + KI	–534	58	125	45	83.43
MOAT					
100	–544	190	120	45	45.71
400	–530	120	130	60	65.71
1000	–522	88	125	50	74.86
400 + KI	–534	60	130	50	82.86
BOAH					
100	–548	170	120	55	51.43
400	–544	120	120	60	65.71
1000	–530	80	124	66	77.14
400 + KI	–528	62	132	68	82.69
OAH					
100	–548	200	110	60	42.86
400	–546	130	120	60	62.86
1000	–520	110	130	65	68.57
400 + KI	–522	70	120	65	80.00

Table V Electrochemical polarisation parameters of mild steel in 1 N H_2SO_4 in presence of different concentrations of macrocyclic compounds with and without KI at 35±2°C

Inhibitor concentration (ppm)	E_{corr} (mv)	I_{corr} μAcm^{-2}	b_c $mvdec^{-1}$	b_a $mvdec^{-1}$	I.E. (percent)
No inhibitor	–580	380	110	55	–
B MOAT					
100	–596	180	110	58	52.63
500	–598	120	115	60	68.42
1000	–572	55	110	55	85.53
500 + KI	–584	37	120	60	90.26
MOAT					
100	–584	220	110	50	42.10
500	–562	140	116	54	63.16
1000	–544	94	120	58	75.26
500 + KI	–548	68	120	60	82.11
BOAH					
100	–582	150	125	60	60.53
500	–586	130	115	55	65.79
1000	–584	76	110	60	80.00
500 + KI	–598	55	116	58	85.53
OAH					
100	–582	200	120	60	47.37
500	–586	180	110	50	52.63
1000	–576	120	120	55	68.42
500 + KI	–600	70	115	58	81.58

213

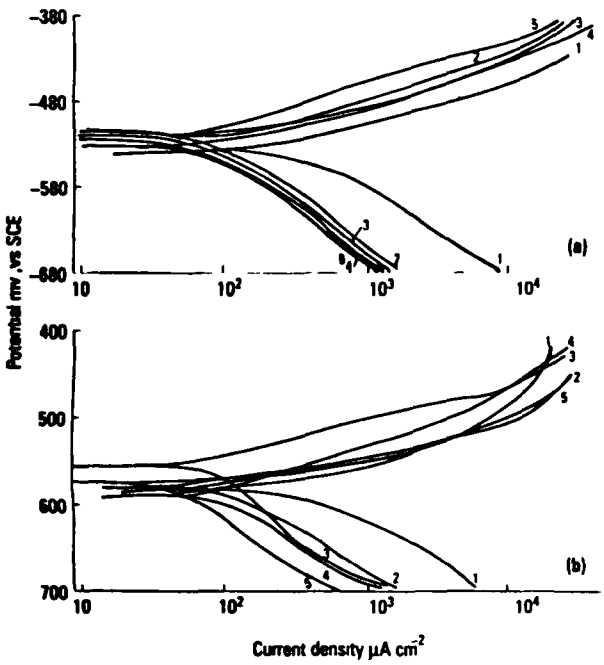
Figure 2 Temkin's adsorption isotherm plots for mild steel in (a) 1 N HCl (b) 1 N H_2SO_4 1 BMOAT, 2 BOAH, 4 OAH



found to obey Temkin's adsorption isotherm.

- Enhancement of inhibition efficiency for all the compounds in HCl as well as in H_2SO_4 in presence of KI showed the synergistic influence of iodide ions on inhibition efficiency.

Figure 3 Potentiodynamic polarization curves for corrosion of mild steel (a) 1. 1N HCl, 2. OAH, 3 MOAT, 4. BOAH, 5 BMOAT, (b) 1 1N H_2SO_4, 2 OAH, 3 MOAT, 4 BOAH, 5. BMOAT



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215